Engineering Sciences

Issues, Opportunities and Researches

Editors

Halil Ibrahim KURT
Engin ERGÜL

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Engineering Sciences: Issues, Opportunities and Researches

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PREFACE

The skills, like critical thinking, communication, analysis, interpretation and discussion in the Science and Engineering are important and continually developing at all stages of life. This book is intended to provide a comprehensive works of the science and engineering studies in a lot of Science and Engineering disciplines. One of the major aims of this book is to present evidence and gathers together the results of research and development carried out on the engineering applications during recent years. It includes discussion of the factors that affect those properties. It is also beyond the scope of this book to provide more than generalized properties- of the different application. The book project brought together scientists and engineers involved in assessing the various engineering areas, with particular emphasis on academic studies, applications and opinions.

Assoc. Prof. Dr. Halil Ibrahim Kurt

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CHAPTER I

SMART GRID RENEWABLE INTEGRATION SECURITY

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1. Introduction

According to developing technologic requirements, power grid system needs major changes. The concept of a "smart grid" refers to the upgrading of current electrical power systems, which includes both central and distributed generation facilities, as well as high voltage transmission lines, to better serve industrial consumers. This modernization also involves the integration of building energy management systems and energy storage components. The integration of various devices such as electric vehicles, home appliances, and applications enables the monitoring of their operations and facilitates automatic optimization to conserve energy. (A B M Shawkat Ali 2013; NIST (National Institute of Standards and Technology) 2014) The smart grid is a novel technological innovation that facilitates the integration of power generation, transmission systems, distribution networks, and consumption. The optimal smart grid should possess a range of characteristics, including adaptability, accessibility, interactivity, predictiveness, integrativeness, and optimization. A smart grid is also sophisticated system that effectively manages the operations of various stakeholders such as generators, consumers, and hybrid users to provide cost-effective and dependable electricity supply (Amin and Wollenberg 2005; Unsal et al. 2021)

The Institute of Electrical and Electronics Engineers (IEEE) has established standardization protocols for smart grids. It has been determined that certain procedural and parameter standards are necessary for the optimal functioning of a smart grid, ensuring that all units including generators, distribution systems, and consumers operate in a cohesive manner. The Institute of Electrical and Electronics Engineers (IEEE) is responsible for establishing standards for devices and systems in order to advance the field of electrical engineering. These standards facilitate the development of products and systems, ensuring that they operate cohesively. The graphical representation depicted in Figure 1.1 illustrates the various IEEE standards and their corresponding applications. The utilization of IEEE communication standards, specifically IEEE std 1901 and IEEE std 802, is prevalent in the context of smart grid applications (NIST (National Institute of Standards and Technology) 2014)

As a result of the current research, the "smart grid" can be characterized as a power system that is highly efficient and dependable, consisting of numerous transmission and distribution grids that are interconnected and communicate with one another. This system is equipped with control and monitoring mechanisms that are interconnected, and can be adjusted to accommodate new systems.

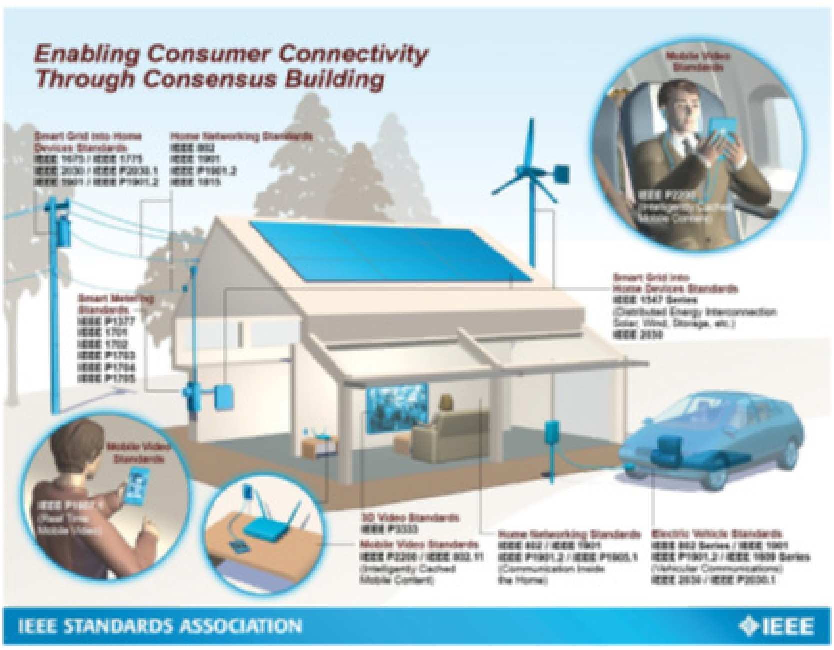

Figure 1.1 IEEE standards and their corresponding applications.

Enhanced security and dependability of intricate systems can be achieved through the utilisation of real-time communication protocols. These protocols facilitate the alteration of system control information across various stages, including generation, transmission, distribution, and end-users within the network architecture (Aoufi, Derhab, and Guerroumi 2020; Unsal et al. 2021)

Upon the development of the smart grid, a multitude of intelligent assets with communication capabilities will be incorporated into the existing electrical grid infrastructure. The aforementioned scenario gives rise to novel security challenges concerning conventional electrical grids within expansive regions (Alvaro Cárdenas 2012). Hence, the subject of smart grid communication technologies holds significant importance in terms of security. Nonetheless, the integration of smart grid technology within residential settings poses a significant concern as any security breaches or faults may result in substantial damages (Amin et al. 2015; Aoufi et al. 2020).

One of the most crucial areas of concern pertains to safeguarding the privacy of personal information within our households, such as consumption patterns, billing records, and related data. Therefore, it is imperative for certain governments to implement precautionary measures (Amin et al. 2015) There is a significant amount of research available on the topic of ensuring security in the implementation of smart grids.

2. Renewable Integration Security

Numerous methods of electricity provision exist that aid in the mitigation of carbon emissions on a smart grid. One potential strategy is the reduction of greenhouse gas emissions in network operations, while another approach involves integrating renewable energy sources such as solar or wind power into the grid through edible plant connections. Reducing the usage of regulators can lead to a decrease in the environmental impact caused by network operators (Refaat et al. 2021). The implementation of smart grid technology in the United States has the potential to reduce carbon emissions by 25%. Conversely, with regards to carbon dioxide emissions, it has the potential to facilitate the maintenance of cleaner air across a land area of 160 million hectares of forest. This implies the inhalation and exhalation of gaseous substances by an estimated 130 million arboreal organisms. The implementation of a smart grid also yields positive outcomes (Hussaini and Majid 2014; Refaat et al. 2021)

Long-term economic growth projections indicate a potential increase of 3.5% in the global economy. This growth, coupled with industrialization and urbanisation, has led to a substantial rise in the demand for natural resources and energy (Anon n.d.) It has been indicated that if current energy policies continue, the world's energy demand in 2035 will experience an annual average increase of 1.5%, resulting in a 46.7% increase compared to the levels observed in 2010.

Consequently, the challenge of accommodating this expanding growth while minimising carbon emissions can be addressed through the integration of dependable energy sources into the system. Upon analysing the energy supply in Turkey, based on the latest available data from 2011, it is evident that natural gas holds the highest share at 32.2%, followed by coal at 31.3% and oil at 26.6%. The remaining 9.9% is primarily sourced from hydraulic energy and other forms of renewable energy. Upon conducting a comparison of the years between 2009 and 2011, it was observed that the proportion of primary energy supply derived from natural gas and wind sources had increased. Turkey is a nation that is highly reliant on imported energy resources, with imports accounting for 71.8% of its energy supply in the year 2011 (OECD-FAO 2021). The limited availability of renewable energy sources and the reliance on energy imports have a direct impact on the financial burden borne by consumers. The incorporation of renewable energy resources into the network has the potential to reduce consumer payments, as evidenced by available data (Sachs et al. 2018).

The integration of renewable energy sources into smart grids necessitates enhanced power flow capabilities that enable bidirectional communication. Various communication capabilities can be utilised by networks to accomplish this task. Upon analysing characteristics of networks with varying communication abilities, one example is Wide Area Networks (WANs), which serve to connect communication infrastructures across different regions of a nation or function as a public service (Alimi, Ouahada, and Abu-Mahfouz 2019)

Local Area Networks are typically utilised within a singular personal area. In contrast to other networks that can be categorised based on their geographical coverage, LAN operates as a peer-to-peer communication network that facilitates point-to-point and point-to-multipoint communication among its users without necessitating communication with any intermediary switching nodes. Communication within a local area network (LAN) is characterised by high data rates and minimal transit delays, typically on the order of a few milliseconds or less (Institute of Electrical and Electronics Engineers. 2011)

According to scholarly sources (Alimi et al. 2019; Institute of Electrical and Electronics Engineers. 2011; Refaat et al. 2021), a Metropolitan Area Network (MAN) is designed to cover a larger geographic region compared to a Local Area Network (LAN). Metropolitan Area Networks (MANs) have the capability to establish communication channels that facilitate high data rates similar to those of local networks. While a MAN can be privately owned and managed by a single organisation, it can also be operated as a public service, catering to the needs of multiple individuals and organisations. Building Area Networks (BANs) are a type of network utilised within buildings. It may be posited that each level is equipped with distinct building area networks (BANs) that are interlinked through a local area network (LAN). A LAN-structured network that is exclusively utilised within residential settings is referred to as a Home Area Network (HAN). Neighbourhood Area Networks (NANs) refer to a network infrastructure that comprises numerous interconnected Home Area Networks (HANs) within a specific geographical location, facilitating the exchange of data among them. NAN has the capability to provide measurement data to data collectors and facilitate the management of HANs. Industrial Area Networks (IANs) are utilised in industrial settings, similar to the operation of Local Area Networks (LANs). In addition to their various usage areas, Industrial Area Networks (IANs), Home Area Networks (HANs), and Building Area Networks (BANs) can be implemented as either wired or wireless networks within customer premises such as homes, buildings, and industrial areas. These networks facilitate communication between various appliances, including Advanced Metering Infrastructure (AMI), power electronics, energy management devices, other smart applications, and end-users. The utilisation of Home Energy Management Systems (HEMS) or other energy management systems may serve as the impetus for applications and communications within these networks.

Although several of these terms lack official recognition, they are frequently utilised in the context of applications.

The infrastructure of the power grid comprises of various components such as generation, transmission, and distribution substations. The categorization of cybersecurity can be delineated into three distinct systems, as illustrated in Figure 2.1:

The category of smart infrastructure systems encompasses smart energy, information, and communication systems. It is imperative that they operate in tandem with the intelligent management system and provide reinforcement to its safeguarding mechanism. Cybersecurity solutions currently available encounter challenges in fulfilling the requirements of communication systems in the context of SG. Upon examination of recent research, it can be discerned that conventional cybersecurity techniques and algorithms have been the focus of investigation, while separate inquiries have been conducted on the topics of power and communication in relation to cyber threats. The presence of cybersecurity risks in critical systems, such as power system communication infrastructure, can result in significant consequences. As a result, conventional risks are now incorporated into risk assessments.

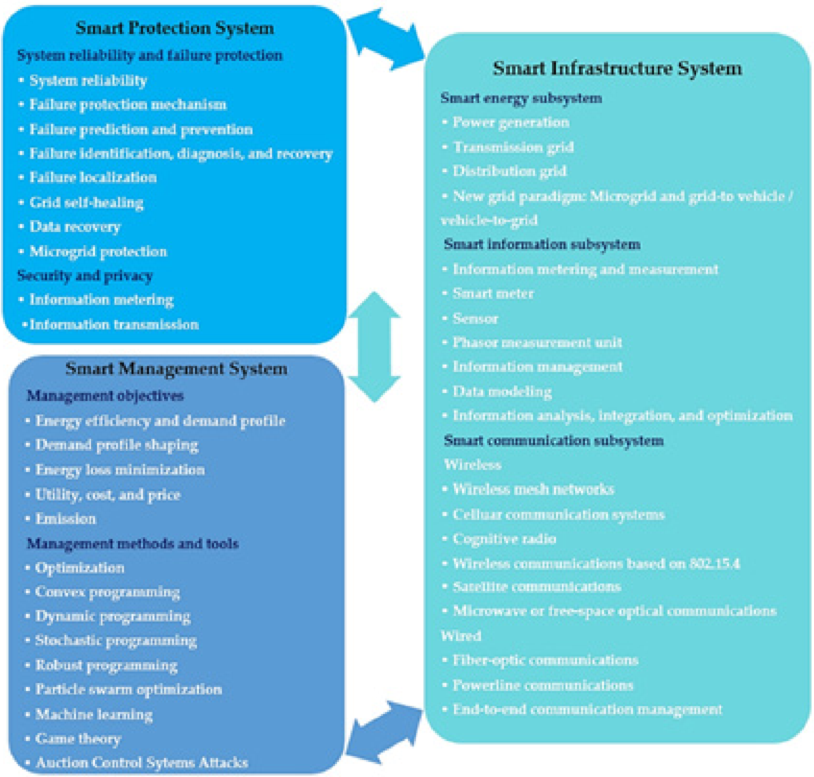

Figure 2.1. The structure and relationship diagrams of the cyber-security system in SG (Unsal et al. 2021)

3. Cybersecurity in Smart Grids and Requirements

This section concerns itself with the identification and analysis of cybersecurity vulnerabilities that exist within smart grids, as well as the necessary mitigation requirements. The SG system is designed to automatically adjust the functionality of electrical power and communication systems in order to optimise their operation. The term SG is characterised as the shift from current power systems to forthcoming systems that rely on information, transmission, and communication technologies. Its primary objective is to oversee all components to avert potential attacks, as cybersecurity is of paramount importance in this context (Alvaro Cárdenas 2012). The essential data can be comprehended such that all potential security hazards within the system can be safeguarded through appropriate measures. Within this particular context, it would prove advantageous to analyse various studies in order to gain a comprehensive understanding of the necessary mitigation requirements.

The current studies conduct an analysis of the security considerations pertinent to the Smart Grid (SG), with a particular focus on the Internet of Things (IoT) and the various forms of cyber threats that pose a risk. Additionally, the environmental factors that impact the cybersecurity of the SG are categorised into three distinct groups.

This study focuses on the vulnerabilities of power grids during cyber-attacks, particularly on the ease of breaching the control system. Additionally, the investigation delves into the factors that contribute to the facilitation of control over the management system.

The process of cyber-attacks can be divided into three distinct stages. The initial stage involves the perpetrator's intention to gain control over the management and communication infrastructure. Upon obtaining management access, the perpetrator must proceed to discern the appropriate system to launch a sophisticated and efficacious malevolent assault. During the third phase, the perpetrator initiates the takeover of the SG component or endeavours to exert influence over its functioning. The attacks have the potential to target either power systems equipment (Almalawi et al. 2014) or auxiliary systems, including Advanced Metering Infrastructures (AMI) (Alimi et al. 2019). The presence of security vulnerabilities within power and communication protocols can potentially lead to hazardous attacks on the SG system. Upon analysing the substance of the implemented standards with the aim of mitigating this issue, it becomes apparent that they rely on technologies pertaining to authentication, encryption, and confidentiality in order to safeguard the security of SG. Individuals with malicious intent may have a vested interest in initiating extensive assaults on the smart grid, which could result in unforeseeable ramifications. Given these concerns, security emerges as a paramount issue in both the ongoing development and future deployment of the SG (Aoufi et al. 2020). The significance of cybersecurity in SGs is depicted in Figure 3.1.

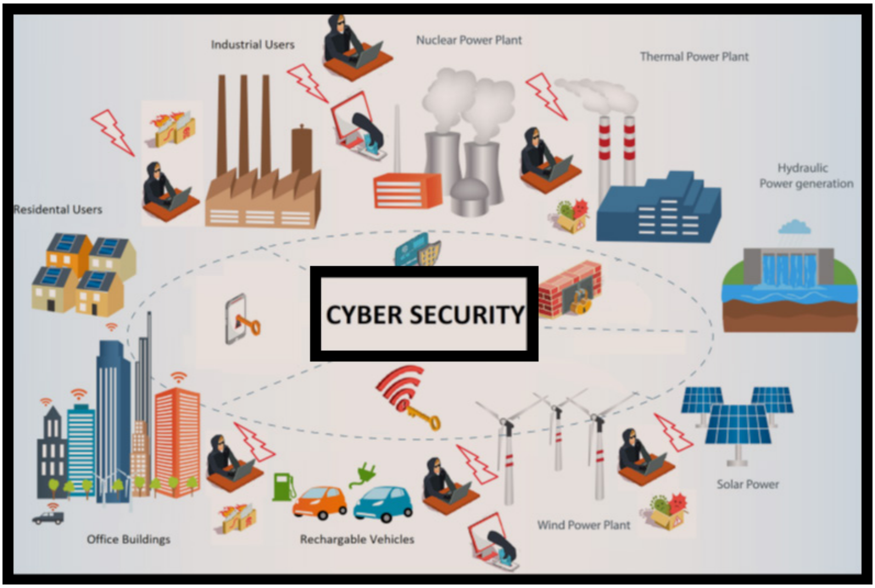

Figure 3.1. The significance of cybersecurity in SGs with renewables (Unsal et al. 2021)

3.1. Cyber Security Issues of Smart Grid

"Cyber-Physical Systems" (CPS) is intricately linked with modern terminologies such as Industry 4.0, Internet of Things (IoT), Machine-to-Machine (M2M), the Internet of Everything, TSensors (Trillion Sensors), and the Fog. This perspective encompasses the idea of technology that encompasses both the physical and digital realms (Alimi et al. 2019).

The acronym "cyber" refers to discrete, logical, and switched processes that are computed, communicated, and controlled. On the other hand, the term "physical" signifies that systems are governed by the principles of physics and operate in a continuous manner. The term "Cyber-Physical" (CP) pertains to systems that demonstrate a significant level of integration between their cyber and physical components across diverse environmental conditions and levels.

The system known as SG can be categorised as a conventional CP System, which integrates a physical infrastructure for energy transmission and distribution with digital communication and management processes (Alvaro Cárdenas 2012). As the scope of smart grids (SGs) broadens, there will be an integration of numerous intelligent assets that possess bidirectional communication capabilities within the system. The aforementioned situation presents new security challenges over a wide geographical area (Alimi et al. 2019; Aoufi et al. 2020). The implementation of real-time communication standards can effectively enhance system security by modifying the control system that interconnects the various components of the network architecture, including generation, transmission, distribution, and consumers.

4. Cyber-Physical Attacks

According to the Electric Power Research Institute (EPRI), all components of Steam Generators (SGs) must operate synchronised and securely. This is indicated by citation (NIST (National Institute of Standards and Technology) 2014; NIST n.d.). It is essential to recognise that ensuring total security requires the implementation of cybersecurity technologies, policies, and risk assessments, as well as a significant component of education and awareness. Numerous studies (A B M Shawkat Ali 2013; Amin and Wollenberg 2005; Anon 1987; Hussaini and Majid 2014) demonstrate that the human factor is frequently responsible for the prevalence of security flaws. By subverting the individuals or organisations in command of the system, it becomes much easier to avoid antivirus software, systems that report cyber attacks, and firewalls. Despite the development and implementation of technical regulations and security policies, the effectiveness of these measures may be compromised by users who are unaware of their existence and disable them. While it may not be possible to eliminate information security vulnerabilities entirely, it is possible to mitigate them to an acceptable degree by nurturing a culture of information security awareness among employees and translating this awareness into actionable steps. The infrastructure sector is highly susceptible to attacks, especially those originating from an internal source that is familiar with the system's complexities. These assaults pose a significant threat to the overall security and stability of the sector. Institutions typically rely on the robust physical security measures of their existing SCADA systems and presume they are impervious to such an attack. Consequently, they are susceptible to significant losses and injury in the event of an assault. Upon the attacker's acquisition of system control, the attack's initiation and execution are initiated. A connection is established with the command-and-control systems after this procedure has been initiated and the malware has been successfully loaded onto the targeted computer systems. This situation enables attackers to remote access.

After gaining remote access successfully, the perpetrators proceeded to elevate privileged accounts, thereby acquiring user credentials (Amin et al.

2015; Anderson 2008). The SG utilises advanced technologies, such as big data, IoT, and cloud computing, to protect the complex CPS security. The term CPS refers to a system that employs advanced computing and communication technologies to monitor and control individuals' physiological functions in the virtual domain. Given the importance of CPS security across multiple domains, it is noteworthy that any assaults could potentially affect both the cyber and physical infrastructure, as indicated in the cited source(Alimi et al. 2019).

Figure 4.1 provides a chronological overview of the various hazards and dangerous assaults that have occurred worldwide over the past two decades. Since 1982, numerous nations have been affected and diverse systems have been damaged. In addition, the consequences of these malicious assaults are delineated concisely.

Undesirable occurrences that may occur within smart grids can be summarised as follows:

The impeded or delayed transmission of data through the network can interfere with control and monitoring operations.

Unauthorised modification of commands, instructions, and alarm thresholds may result in the closure, inactivation, or destruction of system components, posing a threat to the environment, personnel, and other individuals.

By interfering with secure systems, the negative effects of situations that induce operators to issue unlawful commands, such as transmitting inaccurate data to system operators or concealing unauthorised modifications, pose a threat to human lives.

In addition to financial repercussions, CPS attacks can result in the partial impairment of machinery and, in extreme cases, the propagation of failures throughout the entirety of power systems, leading to their complete shutdown.

The attacks can target both the cyber component, which includes the software and communication layer, and the physical component, which includes the electrical power apparatus.

Common attack patterns include a variety of techniques, including man-in-the-middle attacks, rogue device attacks, denial-of-service attacks, and false data injection (FDI) attacks (Unsal et al. 2021), among others. As a generalisation, a variety of dangerous assaults can be classified based on their objectives, intended targets, or outcomes.

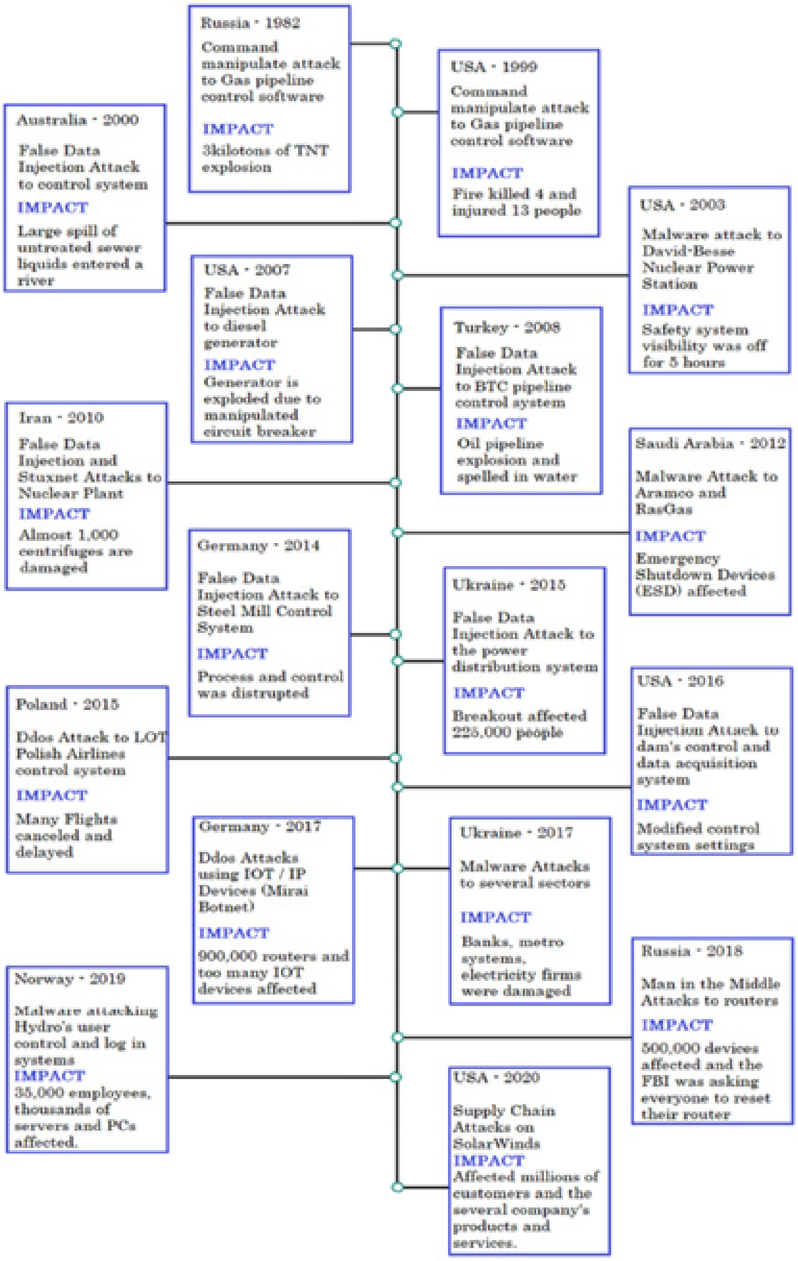

Figure 4.1 Chronological overview of the various hazards in power grids (Unsal et al. 2021).

DoS, which stands for Denial of Service, refers to the act of interfering with or destroying the functionality of a service. Both users are prohibited from accessing and providing extended services by the system. Part of this study will investigate the underlying purpose of the relevant research.

DoS attacks render a system inoperable by saturating it with traffic or requests, thereby exceeding its resource limits. In instances where the attack is confined to a single Internet Protocol (IP) address, a Firewall (Al-Nasseri and Redfern 2007; Almalawi et al. 2014; NIST n.d.) can be utilised as a preventative measure.

Similar to a Denial of Service (DoS) attack, Distributed Denial of Service (DDoS) attacks are implemented in cybersecurity with the intent of disrupting or rendering a service ineffectual of providing its intended functionality. The perpetrator created the malicious software in advance of the targeted attack on the computer or computer network. Nevertheless, the perpetrator can easily conceal their actual identity while remaining concealed. Unlike a Denial of Service (DoS) attack, a Distributed Denial of Service (DDoS) attack employs multiple machines, making IP detection a more complex process. DDoS assaults are more dangerous and potent than DoS attacks because a firewall's adequacy may be insufficient. In addition, Distributed Reflective Denial of Service (DRDoS) resembles DDoS and employs additional networks to conduct attacks more frequently (Alvaro Cárdenas 2012; Ashok and Govindarasu 2012; Hasan et al. 2023; Otuoze, Mustafa, and Larik 2018).

Cathegory of packet sniffing attacks is designed to intercept and extract the contents of data transmissions within a network. The practise of intercepting and analysing data traffic is known as sniffer. An attacker's objective is to intercept and retain all information exchanged between two parties by observing the network's communication traffic.

Another attack type is MitM (Man-in-the-Middle Attack) and there are three entities involved in a (MitM): One perpetrator and two targets. At the onset of the assault, the perpetrator sends signals to the initial victim system, fraudulently identifying it as the second victim system, while simultaneously sending signals to the second victim system, falsely identifying it as the first victim system. The initial target sends all packages to the perpetrator, who then uses the MitM technique to forward them to the second target. The individual under duress believes they are utilising a typical network connection after a false connection has been established. Frequently, these attacks are carried out by exploiting the Address Resolution Protocol (ARP) by manipulating the MAC address data via ARP poisoning. Alongside the expansion of internet networks, there has been an increase in security flaws. Since the vulnerability in the Address Resolution Protocol (ARP) was identified roughly three decades ago, it has been patched. Despite this, compromising computer systems remains a prevalent practise. According to previous research (Alimi et al. 2019; Anderson 2008; Aoufi et al. 2020; Ashok and Govindarasu 2012), the results indicate that the implemented security measures were inadequate. The prevalence of mobile networks, which enable uncomplicated joining and exiting, heightens the difficulty of preventing ARP poisoning and MitM assaults.

The provision of Internet Protocol (IP) connectivity between computers is facilitated by a variety of protocols. After establishing a connection with another computer via said protocols, the connected system reveals its identity to the other computer. IP masquerading is a technique used to conceal the true identity of a connected computer by modifying its displayed IP address. The computer that receives the fraudulent IP packet is unable to ascertain the packet's origin, rendering it impotent of determining whether the packet was transmitted from the actual source address. Theoretically, it is possible to connect to another person's computer from a different IP address. However, in practise, this is unlikely to be accomplished unless the receiving system is seized. Commonly, deception is used to conceal the source of an assault(Alvaro Cárdenas 2012; Aoufi et al. 2020; Ashrafuzzaman et al. 2018; Unsal et al. 2021).

When this study focuses on Command Manipulation Attacks, typically, such assaults are directed specifically at servers, unlike SQL injection. The command line of the web application enables remote access to information about the operating system, database management system, and server. There are numerous applications, such as Code manipulation and Database manipulation assaults, which are classified according to their usage (Ashrafuzzaman et al. 2018)

Another attack called the phenomenon known as "Chameleon Attacks" is of interest to the cybersecurity community. In multi-user systems, the "chameleon" functions similarly to a conventional programme and employs various deceptions and ruses to store credentials and passwords. This is accomplished by its ability to simulate a confidential file and issue a notification regarding the system's temporary closure for maintenance.

The use of the Chameleon programme requires the retrieval of a confidential file in order to acquire identities and passwords.

Keylogger Intrusion Incidents act as key recorders are software applications that secretly record and store keystroke information. The user may be oblivious that their keystrokes are being recorded and transmitted to predetermined destinations when practicable. The use of software that logs keystrokes highlights the potential risks associated with the disclosure of private user information.

Incidents of Unauthorised Access through Hidden Passages in Computer Systems attack techniques enable remote access. It can circumvent conventional computer authentication procedures without being detected. Individuals who engage in hacking with the intent of infiltrating a system typically seek to establish a more expedient means of accessing said system. Maintaining an open port on the targeted system in conjunction with an eavesdropping agent is a common technique for constructing a backdoor.

Backdoor attacks typically involve malicious software that can infiltrate a target system covertly. When a computer is infected with numerous viruses, it is common for these viruses to attempt to open a gateway. Those with malicious intent and knowledge of this circumstance are capable of exploiting these structures. Microsoft allegedly installed a backdoor for the U.S. National Security Agency (NSA) in every version of the Windows operating system, according to a commonly held belief regarding the backdoor. The aforementioned assertion relates to the NSAKey auxiliary input mechanism, which is incorporated into the CryptoAPI infrastructure present in all versions of Microsoft software (Amin et al. 2015; Aoufi et al. 2020).

Supply Chain Vulnerabilities can be called as an assault may include any techniques that align with the system's precision prior to its execution. Recent statements suggest that when the supply chain requires sophisticated protection against attacks, numerous foreign network devices may contain back doors that allow unauthorised access by malignant actors [100]. Supply chain attacks can be carried out without a hacker's physical access to the system. The domain of supply chain management is also intertwined with the need to ensure confidence in system enhancements and components utilised in heightened cyber attacks (Alvaro Cárdenas 2012).

The primary purpose of Spyware and Malware Attack called as software applications, which do not meet the full definition of viruses, is to collect data from the host computer and send it to the programmers. This software's potential hazard to computer or control systems may vary based on its level of surveillance, and it may be viewed as less malignant than other forms of pernicious software. In contrast, the derivatives that pose the greatest danger are capable of obtaining user data through data manipulation.

Trojan Horses term refers to a type of computer software that appears to serve a beneficial purpose but conceals potentially harmful functions capable of evading security measures and, in some cases, exploiting the legal authority of a control and communication system unit (Gunduz and Das 2020; Mo et al. 2012). Given the possibility of confusion, it is advantageous to highlight the characteristics that distinguish viruses from Trojans, Worms, and Stuxnet.

Trojans are apparently harmless programmes that do not interfere with system operation. In the event of a particular circumstance, however, they will be used to exploit opportunities for other criminal purposes.

Worms are self-replicating software entities with the ability to spread throughout computer networks. It should be noted, however, that a virus is not capable of infecting a system on its own. Through the process of attaching itself to additional files, the virus spreads. Noteworthy is the fact that the virus cannot spread to other environments if the infected file remains unopened (Otuoze et al. 2018).

Stuxnet modifies the Ladder logic code of Programmable Logic Controllers (PLCs) and propagates through USB devices (Ashrafuzzaman et al. 2018).

Rogue Device Attacks provide a favourable opportunity for malicious actors to engage in supply chain attacks, in which they can reintroduce malicious software into a device prior to its shipment to a designated destination and then use it to execute a backdoor attack (Aoufi et al. 2020; Otuoze et al. 2018).

False Data Injection Attacks (FDIA) purpose to inject malicious measurements and alter the results. The FDIA could compromise data integrity in multiple domains, including transmission, communication, generation, and control.

5. Conclusion

The study provides an overview of the cybersecurity vulnerabilities of smart grids. It can investigate the integration of information technologies with power systems, which has created new and unprecedented challenges. The documentation of mitigation requirements is subsequently addressed in numerous standards and scholarly publications. These study provides a thorough analysis of potential cyber threats that may target smart grids, with a focus on fraudulent data injection attacks. Due to their propensity to substantially impact the power system’s operation, the aforementioned assaults are handled differently. Also it can provide a comprehensive overview of the extant literature on identifying fraudulent data injection in the context of the smart grid.

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CHAPTER II

MICROALGAE FOR ECOPOIESIS: APPLICATIONS IN SPACE STUDIES AS SUSTAINABLE AND RENEWABLE RESOURCES FROM PAST TO FUTURE

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1. Introduction

Human beings have been curious about the nature of objects seen in the night sky and the mysteries of space since ancient times. Different civilizations used the stars for various activities, such as predicting the weather, agricultural activities and religious ceremonies. The ancient Sumerian, Egyptian, Babylonian, Aztec and Greek civilizations, created lunar and solar calendars. In the following centuries, Eastern and Western civilizations influenced one another with their scientific research into astronomy and space, and produced eminent scientists in these fields. The aim of the research carried out during this time was to determine the dates of religious festivals, to meet the increasing navigational needs of mariners and to solve problems related to the calendar.

From this period until the 20th century, astronomical knowledge increased both experimentally and theoretically, and applied sciences began to replace the predictions of ancient times. The space race in the shadow of the Cold War had a major impact on 20th century space research, and many technological advances were registered in this period.

"Sputnik 1", the first artificial satellite, was sent into space on October 04, 1957, by the Union of Soviet Socialist Republics, and is considered a milestone marking the beginning of the space age. The door to the exploration of outer space was thus opened. The telescopes, spacecraft and space stations developed as a result of scientific research since the first artificial satellite was sent into orbit have yielded much more data about space. Subsequent space missions have been implemented and conducted in the light of this acquired knowledge and experience.

This review discusses studies and the potential for using algae in space missions as sustainable and renewable resources during space research and space travel. It was designed to include information on the importance and uses of microalgae as sustainable and renewable resources, a brief history of algae research in space and algae-based life support systems as pioneer organisms for the creation of ecosystems capable of supporting extraterrestrial life.

2. The Importance and Applications of Microalgae as Sustainable and Renewable Resources

Algae inhabit a wide variety of aquatic ecosystems, such as marine and fresh water, extreme environments, such as snow and glaciers in the Arctic and Antarctic, and terrestrial habitats. They represent a group of prokaryotic and eukaryotic photoautotrophic organisms capable of converting nitrogen and phosphorus into biomass using light energy and CO_2 through photosynthesis (Babich et al., 2022).

Algae are classified according to their pigments, photosynthetic storage products, organization of photosynthetic membranes and other morphological features. They can be divided into microalgae, mere microns long, and macroalgae, up to tens of meters in size. In terms of size, algae range from 0.2 – 2.0 mm to 60 m-long leafy giant algae. Macroalgae include red (Rhodophyta), green (Chlorophyta), and brown algae (Ochrophyta) and are mostly found in marine ecosystems. Microalgae are represented as green (Chlorophyta), blue-green (Cyanobacteria), yellow green (Ochrophyta and Xanthophyta) and gold (Ochrophyta and Chrysophyta) algae and diatoms (Bacillaryophyta). Green algae synthesize important secondary metabolites through their pigments, the main storage compound being starch and lipids. Diatoms represent the largest group of biomass and oxygen producers, the majority of which are found in marine ecosystems, but which can also be seen in fresh water. The cell walls of diatoms contain largely polymerized silica. Golden algae are microscopic, unicellular biflagellates with two specialized flagellae. Cyanobacteria differ from other bacteria in that they possess the ability to perform photosynthesis with oxygen and to exist in a wide range of temperatures and salt levels. Since Cyanobacteria release oxygen through photosynthesis, they are considered to be the first colonizers on Earth, enabling other life forms to live on the planet. There are estimated to be between 50,000 and 80,000 different microalgae species exhibiting a wide variety of different characteristics (Enzing et al., 2014; Klinthong et al., 2015; Chu, 2012; Sigamani et al., 2016).

Algae have long been used as a food source in Far Eastern countries such as China, Japan and Korea. Micro and macroalgae have been employed as potential candidates for helping meet the protein needs of the growing world population since the 1950s. Large-scale commercial microalgae cultivation started with *Chlorella vulgaris* species in the 1960s, followed by *Arthrospira* (*Spirulina*) species in the 1970s. Microalgae production facilities have been established in countries such as the USA, India, Australia and Israel since 1980 (Spolaore et al., 2006).

Since algae can be found in large quantities in aquatic ecosystems, are easily cultivated, and enjoy a wide area of use they have recently become important organisms in the context of climate change, sustainable green economy and alternative energy sources (Enzing et al., 2014). The fact that waste biomass is poor in lignin and rich in secondary metabolites allows these biomasses to be used in fields such as nutritional supplements, animal feed, fertilizer and pharmaceuticals (Razzak et al., 2013; Gonçalves et al., 2013). Numerous species of microalgae grown in the laboratory are used as model organisms in natural sciences to elucidate and clarify the mechanisms of respiration and photosynthesis, and the biosynthesis of biochemical compounds.

Microalgae species are a source of protein, lipid, carbohydrates, several vitamins and macro and microelements and have a high-energy value (Martínez-Hernández et al., 2018). These compounds synthesized by microalga include polyunsaturated fatty acids (PUFAs), sterols and steroids, polyphenols, polysaccharides, carotenoids, lectins, amino acids, proteins, halogenated compounds, alkaloids, alginic acid and carrageenan. Some strains contain high concentrations of ω6 and ω3 PUFAs due to environmental and nutritional factors. Microalgae are also rich in A, B_1, B_2, B_6, B_{12}, C, E, folic acid and pantothenic acid, biotin, nicotinic acid and phycobiliproteins. Various studies have shown that these exhibit therapeutic properties such as anti-inflammatory, antitumor, antiviral, antibacterial, antifungal and anticoagulant activities (Singh et al., 2017(a); Forján et al., 2015). The use of microalgae for pharmaceutical purposes and medicinal applications has led to the discovery of new bioactive compounds. The bioactive molecules obtained from microalgae include carotenoids, alkaloids, phenolic compounds and terpenoids (Palozza et al., 2009).

Arthrospira platensis, a filamentous Cyanobacterium, and *Chlorella vulgaris*, single-celled green algae, are important commercially produced microalgae due to their high protein content (Andreeva et al., 2021). *Spirulina* and *Chlorella* are sold directly as dietary supplements, being subjected only to drying after growth. Astaxanthin obtained from *Haematococcus pluvialis* is used as a dietary supplement and food additive (Milledge, 2012). β-carotene obtained from *Dunaliella salina*, is employed as a food supplement due to its anti-inflammatory effect and phycocyanin obtained from *Porphyridium* is used as food pigment reagent, Eicosapentaenoic acid (EPA) obtained from *Nannochloropsis, Phaeodactylum* and *Nitzschia* and docosahexaenoic acid (DHA) obtained from *Schizochrytium* and *Cryptocodinium* are also used as food supplements (omega-3 fatty acid, brain development in children and cardiovascular health) (Spolaore et al., 2006).

Secondary metabolites obtained from microalgae species are today used in agricultural applications such as feed additives and fertilization processes in cattle and poultry and on fish farms. Among the most commonly, used species in these applications are *Spirogyra, Scenedesmus, Chlorococcum,* *Nostoc, Nitzschia* and *Navicula*. Additives included in feeds and obtained from microalgae have been found to improve the immune systems of farm animals and to increase fertility rates and pup weights. In addition, an increase in egg production and enhancement of the size and colour of egg yolk have been observed in poultry farms. In aquatic environments, microalgae form the first link of the food chain and play a vital role for many species of crustaceans, molluscs and fish. Many diatoms, flagellates, green algae and blue-green algae species are used in aquaculture. These microalgae species contain high levels of protein and unsaturated fatty acids necessary for the growth and development of many larvae (Forján et al., 2015; Priyadarshani & Rath, 2012). Following the establishment of recycling systems in farms, it was realized that animal wastes could be used for the cultivation of algae and again as feed and fertilizer. Microalgae such as *Chlorella vulgaris, Scenedesmus obliquus, Scenedesmus quadricauda* and *Nostoc* are also used to replenish organic matter stocks such as humic acids that help increase soil fertility (Dineshkumar et al., 2020).

Biomass obtained from microalgae is regarded as one of the most important sources of renewable energy, and its potential uses are attracting increasing attention. These metabolites can be used as raw materials for biofuels such as biodiesel, biogas, biohydrogen, bioethanol and butanol (Peng et al., 2019). Although the oil content obtained from microalgae varies according to the species, the figure lies somewhere between 12% and 70% of their dry weight, and its use for biodiesel production is more advantageous compared to other crop plants. Research into biodiesel production technology from microalgae seems to have overcome technical and economic constraints, thus permitting an increase in production and reduction of final production costs (Chisti, 2007). Microalgae also offer economic and ecological advantages in biodiesel production compared to terrestrial plants due to their high production and photosynthetic efficiency in waters with a wide variety of chemical compositions, and to the fact that they do not require large amounts of arable land for their cultivation.

Microalgae are also regarded as potential organisms for applications in space, and it is predicted that they will play a leading role in space research alongside other organisms, similarly to the areas described above.

3. A brief History of Research with Microalgae in Space

The "Korabl-Sputnik 2" spacecraft was launched by the Soviet Union on 19 August, 1960, at the dawn of the space race. *Chlorella pyrenoidosa,* one type of microalgae, was also on board, along with various other biological organisms.

This mission lasted 25 hours in total, including launch, landing and a short stay in space. *C. pyrenoidosa* cultures were grown in two different groups, the first group on agar plates in the dark, and the second under periodic light and in liquid medium. Due to the brief duration of this first mission, the evaluation of parameters such as culture reproduction, photosynthesis rates and survival was also limited. The results obtained revealed that the cultures sent into space had a higher number of dead cells and a lower photosynthesis rate than the ground controls. It was therefore concluded that *C. pyrenoidosa* cultures sent into space can perform basic physiological processes such as photosynthesis, growth, development and reproduction (Alexandrov, 2016; Niederwieser et al., 2018a).

The Soviet spacecraft Cosmos 110 was launched into space by the Voskhod rocket on 22 February, 1966. This vehicle also carried cultures of *Chlorella* coded as LARG-1 and LARG-3. This mission differed from the others in that the craft remained in orbit for 22 days before landing back on Earth. The frequency of occurrence of visible mutations was examined, and no significant difference was observed compared with the control group on the ground (Shevchenko et al., 1967; Antipov et al., 1969).

Known as the Zond mission between 1968 and 1969, the Zond 5, Zond 6 and Zond 7 spacecraft flew in orbit around the Moon. *C. vulgaris* cultures remained on solid agar plates for six to seven days in dark conditions in all three craft. All previous experiments were performed in Low Earth Orbit (LEO), but this mission went beyond the radiation-shielding Van Allen belts. This caused the algal cultures to be exposed to both deep space radiation and radiation trapped in the Van Allen belts during the spacecrafts' passage. The results when cultures from space were compared with the control groups were inconsistent. Researchers suspected that the discrepancies detected in the results were due to an inability to fully distinguish the effects of radiation and microgravity in the samples. While the cell viability of *Chlorella* cultures were lower in Zond 5 and Zond 6, the researchers reported that space had no effect on cell viability in the experiment in Zond 7 (Vaulina et al., 1971; Anikeeva & Vaulina, 1971; Galkina & Aleksandrova, 1971; Galkina & Meleshko, 1975).

Various different strains of *Chlorella* and *Scenedesmus obliquus* were used in experiments in the Salyut 6 station (1977 and 1982) built by the Soviet Union. Cultures were grown on both liquid and solid media for 4 to 18 days. Findings from post-flight analyses of cultures grown on the space station, a microgravity environment, showed that weightlessness did not affect the increased algal population or the relationship between algae and their environment (Setlik et al., 1978; Alexandrov, 2016; Niederwieser et al., 2018a).

A wide variety of research has been carried out on algae in space since the 1980s. While some has not yielded clear results, some has been successful and provided valuable data about the physiological behaviour of algae in space conditions. Heterotrophic experiments designed using bacteria, fish and algae on the Cosmos missions showed that it is possible to use a small-scale life support system for up to 13 days (Popova et al., 1989). The longest experiment using active microalgae cells were conducted on the Mir space station over a 12-month period. Photosynthetic activities and secondary metabolite formation capacities of *C. vulgaris* cultures were investigated (Sytnik et al., 1992). Experiments using different algae were conducted at the external EXPOSE facility of the International Space Station (ISS). Cells of *Chlorella, Rosenvingiella* and Cyanobacteria *Gloeocapsa spp.* were reported to survive for one and a half years under dark conditions and exposure to a vacuum. *Chroococcidiopsis* cells also survived in the same EXPOSE facility, which included exposure to both outer space and an extraterrestrial UV spectrum in experiments on (ISS) (Cockell et al., 2011). Since 2010, on-Earth experiments exceeding six years in duration have been conducted using *Chlorella* cultures for long-duration space missions at the University of Stuttgart's Space Systems Institute (IRS). These studies include two experiments exceeding 180 days in duration in a microgravity-adapted reactor and hardware development for space applications (Detrell, 2021).

Free-flying satellites and space stations in LEO have yielded a wealth of new knowledge and experience concerning the evolution of organic and biological materials in space and planetary environments. The NASA Long Duration Exposure Facility (LDEF) was an exposure facility launched in April 1984. It remained in space for 2107 days and involved a number of spore and tomato seed survival experiments (Kahn and Stoffella, 1996). The European Retrievable Carrier (EURECA) was the first European satellite designed for microgravity experiments. EURECA used an exposure setup known as ERA (Exobiology and Radia) to study the survival and evolution of bacteria and organic materials in space over a period of several months (Greenberg et al., 1995).

Various studies of biological organisms were also conducted on the Soviet space stations Salute-6 (1977–1982) and Salut-7 (1982–1991). Experiments were then conducted with both chemical and biological materials for 97 days using an exposure facility known as Perseus Exobiology on the Russian space station MIR (Boillot et al., 2002).

Biopan is a retrievable exposure facility mounted externally on photon-type unmanned recoverable satellites for experiments in the fields of biology, radiation biology, radiation dosimetry and chemical evolution. Various organic molecules, vegetative cells, Cyanobacteria, bacterial spores, plant seeds, lichens, and tardigrades have been exposed to combinations of outer space, solar UV, wide temperature fluctuations, space radiation, and microgravity in LEO and within the Biopan (Demets et al., 2005).

The experiments involved prolonged exposure of experimental samples to extraterrestrial solar UV in LEO space outside the ISS, under a defined atmosphere in EXPOSE facilities (Cottin et al., 2017). The effects of space conditions on organisms such as lichens, Fungi, Cyanobacteria and bacteria were investigated in the EXPOSE-E and EXPOSE-R sections.

Tanpopo is the Japanese Experiment Module on the ISS designed by the Japanese Space Agency JAXA for multi-purpose exposure experiments. The purpose of this mission is to investigate the extraterrestrial transfer of terrestrial microbes as well as possible interplanetary transfers of prebiotic organic compounds to Earth by sample return analyses through capture and exposure panels. In order to carry out this important mission, the system was created from six sub-themes. These themes related to microorganism studies by Yamagishi et al., (2009) are "Undisturbed capture of terrestrial aerosols that may contain microbial colonies in Low Earth Orbit (LEO), prolonged exposure to extremophile microbes in LEO, prolonged exposure of biological organic analog compounds in LEO and capturing organic material-bearing micrometeoroids intact in LEO".

NASA 3U CubeSat Organism/Organic Exposure to Orbital Stresses (O/OREOS) was launched in 2010 in order to demonstrate astrobiological measurement technologies. The SESLO experiment collected data for the survival and metabolic activity of microorganisms during the mission. The Space Environment Viability of Organics (SEVO) experiment was also carried out in O/OREOS. This experiment involved a real-time analysis of the photostability of organic biomarkers (Mattioda et al., 2012).

4. The Prospects of Using Microalgae as Pioneer Organisms in Space Exploration

Human beings' fascination with space started with examining and understanding the stars and using such information for the maintenance of human life as civilizations developed. As technology has advanced, humanity has now started to leave permanent footprints on the solar system. Ever since the launch of the first spacecraft, humanity has sought answers to numerous questions about colonizing, the Moon and Mars, searching for evidence of the basis of life and how the universe first came into being. Trends in research into microorganisms and microalgae in space studies to date have developed in the form of short and long-term spaceflights, the colonization and terraforming of asteroids and planets/satellites, and the use of in situ resources, namely the development of bioregenerative life support systems.

The terms ecopoiesis and planetary engineering are frequently employed in the context of space research and studies. Ecopoiesis literally means the creation of an ecosystem capable of supporting life. In terms of space exploration, ecopoiesis is the creation of a sustainable ecosystem on an inanimate or sterile planet or satellite. Planetary engineering, on the other hand, refers to the development and application of technology in order to influence a planet's environment using methods such as terraformation, seeding, and geoengineering. These two concepts include manned long-duration space flights and the development of bioregenerative life support systems that will allow the colonization and terraformation of planets and the conduct of analog experiments between space flights and Earth. Researchers have therefore focused on concepts and research that preserve the position of autotrophic organisms capable of photosynthesis at the center of these studies.

High plants, photosynthetic algae and Cyanobacteria, primary producers, form the basis of natural ecosystems on Earth. Among these primary producers, microalgae, including Cyanobacteria and Chlorophyta, are critical for the future of space exploration due to their photosynthetic oxygen capacity, rapid reproduction ability and valuable metabolites (Fleming et al., 2014). The growth of microalgae and the increase in their secondary metabolites can be controlled by modifying the light intensity in the culture medium, the properties of the medium, and other conditions. These properties make them ideal test organisms for production and use in space. Microalgae have critical roles in the Earth's carbon and nitrogen cycles, converting N_2 gas into ammonia and producing the majority of atmospheric oxygen (Agrawal, 2012). Oxygen and metabolites produced during the process carried out by these autotrophic organisms are transferred along the food chains and made available to more advanced organisms, thus ensuring the continuity of life on Earth (Arena et al., 2021). Since autotrophs are the main players in the life cycle on Earth, their use in life support systems for human survival and the creation of new habitats in extraterrestrial long-term space missions is perfectly logical (Horneck et al., 2003).

Mars is widely regarded as the most likely planet for colonization and settlement in the foreseeable future. Unfortunately, however, Mars has a strong oxidative atmosphere, low temperatures, low humidity, extremely dry conditions, a high atmospheric CO_2 fraction, and high UV radiation that makes its surface a difficult habitat for life (Ehlmann et al., 2011). Most organisms on Earth have evolved to live in environmental conditions that will carry out their vital stages. They cannot survive in extreme environments such as extremely high or cold temperatures, pH, or the presence of xenobiotics for their vital stages (Varshney et al., 2015). In addition to these factors, there are also very high CO_2 gas levels, the presence of high concentrations of metals, very high levels of ionizing radiation, and even extremophile organisms that have to live in conditions of multiple environmental stresses (Rivasseau et al., 2013). Anhydrobiotes are extremophile organisms that can dry out and become dormant. After drying out, they enter metabolic sleep mode, and resume their active metabolism when water is available. Anhydrobiotes accumulate large amounts of disaccharides, sucrose and trehalose, which stabilize their membranes and macromolecules in the drying state (Rabbow et al., 2012).

Various experiments have been carried out simulating conditions in space and on Mars, including UV and ionizing radiation, on organisms that are resistant to drying, and these have exhibited an extraordinary resistance to radiation. These organisms include lichens, fungi, cyanobacteria, bacterial spores, plant seeds and tardigrades (Cottin et al., 2017). Antarctica is the region with the most extreme conditions anywhere in the world, including dry valleys, very low temperatures, low humidity and a high UV environment. The Atacama Desert in Chile is the most arid place in the world (Thomas et al., 2006). In Antarctica, prokaryotes and eukaryotes (fungi, algae and protists) live in ice, cold water and rocks that protect them from drought and UV radiation. These harsh cold conditions are also found on Europa and Mars. *Chroococcidiopsis*, a Cyanobacterium, can live in porous rocks and on the underside of stones and is found in both the McMurdo dry valleys of Antarctica and the Atacama Desert in Chile. Since this species is highly resistant to desiccation and high salinity, it has been proposed as a candidate for breeding on Mars (Friedmann & Friedmann, 1995). While hot springs, volcanoes, and volcanic vents in many parts of the world create anoxic environments due to high CO_2 levels, low pressure, low temperature and high UV have been detected in regions of high altitude. Even in these extreme conditions, there are life forms that have somehow adapted to these (Thomas et al., 2006).

The selection of algae species in space missions will play an important role in the design of the technologies to be used and the performance of the systems to be installed. Considering that extraterrestrial environments will be highly challenging, pioneer microorganisms would have to possess numerous essential characteristics to survive in them (Thomas et al., 2006). Certain chemical compounds must be present for algae and other autotrophic organisms to grow on Mars (Alexandrov, 2016). No known reserves of organic matter have been found on Mars to date. Therefore, organisms will need to construct their own biomolecules from inorganic components through photosynthesis or chemosynthesis (Thomas et al., 2006). Carbon dioxide, which is necessary for photosynthesis, is abundantly present in the Martian atmosphere, even at low pressure, at a rate of 95%. However, it must also be present in various macro and microelements. Recent research into the surface of Mars has estimated that it contains Fe-, Ca- and Mg-sulphates (Kounaves et al., 2010). The surface of Mars is a highly oxidizing environment, possibly due to reactive oxygen species (ROS) generated by UV (Yen et al., 2000). ROS are considered by-products of the oxygenic photosynthetic metabolism of autotrophs and cause cell death and DNA damage (Huang et al., 2019). It is therefore important to detect precursor microorganisms with strong antioxidant systems in order to detoxify internally and externally produced ROS (Thomas et al., 2006).

Psychrophilic photosynthetic species have attracted widespread attention following the discovery of liquid water on Mars, as they may provide clues to the possibility of life. Studies have also shown that psychrophilic green algae accumulate higher levels of lipids compared to their mesophilic counterparts (Cvetkovska et al., 2017). Psychrophilic photosynthetic microalgae may therefore represent good starter organisms. The existence of stable nitrogen in the form of nitrate has been confirmed on Mars (Hand, 2015). Nitrogen is the most critical nutrient for the lipid metabolism of microalgae. Mars has a very thin ozone layer that varies depending on the season and latitude, resulting in sterilizing doses of UV radiation on the planet surface. The surface of Mars is exposed to significant cosmic radiation because due to the absence of a magnetic field like that of the Earth (Lefèvre et al., 2004). Organisms capable of living there will therefore need to possess mechanisms to resist radiation damage and repair the damage caused. Pioneer microorganisms would also be expected to tolerate osmotic stress and survive drying periods.

Simulation rooms can be built on Earth to study how Earth-based organisms adapt to environments such as the extreme conditions on Mars. These simulations can confirm which microalgae are suitable for making a planet habitable. Mars, one of the planets in the process of ecopoiesis, will likely exhibit conditions similar to those on the primordial Earth. Primitive Cyanobacteria similar to the earliest forms of Cyanobacteria that somehow appeared on Earth would thus be prime candidates for terraformation (Alexandrov, 2016). Ganzer and Messerschmid (2009) investigated the integration of an algae photobioreactor (PBR) into the Environmental Control and Life Support System (ECLSS) in a space station containing six astronauts. The design of a PBR operating under Earth conditions for space research was amended, and a simulation model was created using ELISSA software. In addition to the task of stimulating the air, the performance of PBR as a food production system was also evaluated, and the authors concluded that the results were satisfactory. Thomas et al. (2006) performed a study using five species of Cyanobacteria (*Anabaena, Chroococcidiopsis, Plectonema, Synechococcus* and *Synechocystis*), three Atacama Desert heterotrophic eubacterial strains, and several desert varnish isolates. Survival/growth experiments were conducted using the "SHOT Martian Environment Simulator" to determine whether these potential pioneer life forms are suitable for Mars. Microorganisms were inoculated into Mars-1 soil stimulator samples by exposure to a present-day mixture of Martian atmospheric gases and full-spectrum simulated Martian sunlight. Their preliminary results showed that both autotrophic and heterotrophic experimental organisms can survive in the simulated Martian environment (Thomas et al. 2006). The isolation mission, called the EuroMoonMars IMA (HI-SEAS) (Hawaii Space Exploration Analog and Simulation) expedition by NASA, is designed to simulate conditions on Mars. The HI-SEAS habitat, a dome with food and life support systems, includes space exploration simulation and modeling (HI-SEAS, 2022).

Biological samples cannot be simultaneously exposed to all combinations of space factors in simulations or control experiments on Earth. This can only be achieved with special mechanisms and experiments to be carried out in space. Multiple exposure possibilities can be used for short-term experiments (up to approximately two weeks) in space and long-term experiments (up to approximately six years). Experimental facilities that can be used to study environmental parameters and conditions in space possess facilities such "encompass space vacuum, simulated Martian atmosphere, Martian UV radiation and Martian pressure, extraterrestrial UV radiation or selected UV wavelength bands, different temperatures and temperature cycles, inert gas atmospheres (N_2, Ar), cosmic radiation and trapped radiation" (Cottin et al., 2017).

Space exposure studies have been conducted with various algae species since 1997. Some of these studies are cited below. Cultures of *Synechococcus spp.* were studied on a 10-day space survival mission in Biopan 2 carried by

Foton 11 in 1997. The strain *Chroococcidiopsis spp.* was evaluated for survival at the Foton-M2 Stone 5 facility for 12 days in 2005. In 2007, endolithic Cyanobacteria species aboard Foton-M3 Biopan 6 were the subject of research in space for "survival, shielding by Martian regolith, rock, salt crystals; shielding by cortex and pigments" for 10 days. Studies were conducted with the *Anabaena cylindrica* strain for 1.5 years under "space vacuum, solar UV (>110 nm), simulated Martian atmosphere and UV climate (>200 nm)" conditions in the ISS-Columbus-EuTeF, EXPOSE-E facility between 2008 and 2009, and their responses to "survival, protection, and DNA photoproducts gene activation" were recorded. Between 2010 and 2014, trials were conducted on "survival, protection, and DNA photoproducts gene activation" under "Space vacuum, solar UV (>110, >200 nm)" conditions for *Chroococcidiopsis* and *Synechococcus* strains in the EXPOSE-R facility of ISS-Zvezda-URM-D. In that facility, a *Chroococcidiopsis spp*. strain was tested in terms of "survival, resistance by biofilm formation by Martian regotith and DNA photoproducts gene activation" for an extended period, approximately 1.5 years, between 2014 and 2016, with the provision of "space vacuum, solar UV (>110 nm), simulated Martian atmosphre and UV climate (>200 nm)" conditions (Horneck et al., 2010; Nicholson et al., 2011; Cottin et al., 2017).

5. The Applicability of Microalgae in Regenerative Life Support Systems

Due to the current state of technology, all space stations to date have been in LEO. However, highly sustainable and at the same time renewable technologies need to be developed in order to explore space beyond that point (Ganzer & Messerschmid, 2009). The availability of a reliable life support system, ranging from food, water, and oxygen supply to waste management, is absolutely essential for long-term manned space missions.

A closed spacecraft and space station will not possess an endless supply of O_2 and other vital resources similar to those on Earth, and a system is therefore needed to remove excess CO_2 from the environment and replace it with breathable air. The vital needs of astronauts on the ISS are met by the supplies carried by the spacecraft sent from Earth (Alexandrov, 2016). The conditions created on the ISS are state-of-the-art in space habitats, and the Environmental Control and Life Support System (ECLSS) is currently in service, designed to regenerate cabin air and to recycle water. In addition to the decreasing gravity and increasing radiation inside the modules of the ISS, there is an average high carbon dioxide concentration of approximately 400 ppm, 10 times higher than the ambient levels on Earth (Niederwieser et al., 2018b). The maximum required CO_2 value in the ISS has been determined as ≤0.52 kPa (0.52% or 5,200 ppm per volume) (Fahrion et al., 2021). The high rate of CO_2 in the air breathed by astronauts causes medical problems, from an increased incidence of headaches to visual impairment. Since pure oxygen is highly flammable, spacecraft use gas mixtures similar to the atmosphere on Earth. Standard sea level conditions (21% oxygen and 79% nitrogen) are used for ventilation on the ISS (Niederwieser et al., 2018b). An Oxygen Generating Arrangement, Carbon Dioxide Removal Arrangement, and a Carbon Dioxide Reducing Arrangement are used on the ISS to maintain an appropriate gas balance. These systems use renewable absorbent materials, water electrolysis, and the Sabatier reaction to remove CO_2 and produce potable water, but foodstuffs still need to be shipped from Earth (Fahrion et al., 2021; Brunet et al., 2010). Resupply will become more costly and problematic for flights further away from the Earth. Regenerative and redundant autarchic life support systems will therefore be indispensable in such manned space missions in the future and will meet a significant part of the crew's supply needs (Ganzer & Messerschmid, 2009). Even now, an annual 6.8 tons of water are needed to support the six-man crew on the ISS. Calculations show that this amount will reach 30 tons without any recycling for a manned mission to Mars. It is estimated that the cost of this will correspond to approximately 150 million dollars (Revellame et al., 2021). This high supply mass thus entails considerable costs in future long-term reconnaissance missions. The proposed solution is to create large mass cycles involving the recycling of waste materials in an ECLSS. These three main mass cycles, which will consist of water, oxygen and carbon, will involve steps such as regaining oxygen from carbon dioxide and ensuring the feasibility of food production (Ganzer & Messerschmid, 2009).

As mentioned in the sections above, algae and other photosynthetic organisms form the basis of biological life support systems, although the combined effects of microgravity and radiation on these organisms have still not been fully evaluated (Arena et al., 2021). Today, priority research into bioregenerative life support systems includes the selection and development of suitable potential photosynthetic organisms and engineering studies for the establishment of these systems. The main criteria considered for the selection of algae species include rapid growth and high rates of photosynthesis, as well as the capacity to cope with space-related factors (Wang et al., 2006).

The idea of creating and implementing an ECLSS using algae was first considered by the Soviet Union in the early 1960s. In that research, 0.03 m^3 of oxygen produced using an algae growth apparatus was used for 30 days in an airtight 4.5 m^2 room, and the dry algae biomass obtained was added to the human diet (Ganzer & Messerschmid, 2009). Regenerative life support systems, which are still used in all manned spacecraft and space stations, have various physicochemical properties. In the first years of manned space flights, different physicochemical methods were investigated in this context. Lithium hydroxide (LiOH) cans were used in early space missions such as Mercury, Gemini, the Apollo Command Module and the Apollo Lunar Module. These cans removed CO_2 by converting atmospheric CO_2 into lithium carbonate (Li_2CO_3) (Winton et al., 2016). Researchers have stated that PBRs using algae as hybrid life support systems can be used to provide integration between the physicochemical and bioregenerative life support systems (Alexandrov, 2016).

The designs of the PBR and equipment to be used in bioregenerative life support systems in space studies should be suitable for growing microalgae in a controlled manner. Photobioreactors should be designed to withstand space conditions and will require other sub-systems such as adequate lighting (periodic lighting when necessary), gas exchange, a continuous nutrient supply, harvesting and waste removal, and temperature control, which will provide physical containment of the microalgae (Detrell, 2021). Most of the energy required for space stations is provided by the Sun, and it is imperative that the energy obtained be used very efficiently. Power consumption limitations therefore need to be considered during the design of a PBR. The size of the PBR planned to be installed in space missions is also important in this context and requires the calculation of various parameters. Some of these parameters are the type of algae to be used, the parameters to be applied during cultivation, the rate of biomass production, and the amount of oxygen.

Although PBRs vary depending on their configurations and operating modes, the most frequently used types are flat plate, tubular and columnar. Each PBR type has its own advantages and disadvantages that vary according to various factors. PBRs are constantly being developed in terms of economic efficiency, biomass yield, the size of the reactor, and their optimization according to the environmental conditions where they will be located (Ahmad et al., 2021). Various physical and biochemical factors must be well organized in the design of PBRs in which microalgae will be grown. These factors include pH, nutrients, temperature, mixing, light intensity, predators or invasive species, and the PBR model and design.

pH is one of the important factors affecting the photosynthetic abilities and growth of microalgae. Although it varies depending on the species involved, the optimum pH range required for the growth of microalgae is 6-8. Under Earth conditions, pH rises during the day due to photosynthetic assimilation by microalgae and decreases during the night due to the respiration process. An increase in CO_2 will cause an increase in the amount of biomass, while a decrease in pH will negatively affect microalgal physiology (Huang et al., 2010).

Microalgae need macronutrients such as phosphorus and nitrogen, and trace metals such as Fe, Mg, B, Mo, K, Co, Zn, and Mb in their nutrient medium for growth. Since these nutrients are used in a wide variety of metabolic pathways within the cell, excesses or deficiencies may cause morphological and physiological changes in microalgae (Yalcin, 2020).

The optimum temperature at which microalgae can grow is in the range of 25-30°C, depending on the species. Temperature can be easily controlled in PBR systems, making their use advantageous. Mixing microalgae grown in the PBR is important in order to promote algae movement between the dark and light regions of the system, to prevent precipitation, and to ensure that homogeneous cell concentrations are maintained. The most critical factor in the production of microalgae in PBRs is light intensity. For microalgae, light intensity affects the rate of photosynthesis and the production of biomass and secondary metabolites. The components that affect the light intensity are the PBR type, the density of the microalgae mass and the depth of the culture medium (Yousuf, 2020).

The light intensity for microalgae cultures is usually between 150 and 350 $\mu mol\ m^{-2}\ s^{-1}$, and white, blue, or red lights can be used. The available ambient light intensity provided inside spacecraft is normally outside this range because of energy savings. For this reason, a special lighting system should be provided for microalgae in the design of a PBR to be used in space. The optimal light period used in reactors is usually a 12/12 day/night cycle. A 16/8 cycle is also used as the light period in the cultivation of microalgae, although minimal decreases in productivity may be observed, depending on the microalgae species. Using a flashing light effect can increase the growth rate but this system should be placed in a separate section, as it will cause discomfort to the crew (Niederwieser et al., 2018a).

The major handicap in microalgae cultivation in open pond systems around the world is other microbial contaminations and predators or invasive species. Scientific characterization studies with algae are carried out under axenic conditions in order to eliminate different variants. In studies with axenic cultures, sterile equipment and antibiotics are used and a single strain is inoculated into the growth medium to prevent cross-contamination. While symbiotic interactions of microalgae and some bacteria may be beneficial, parasitic interactions have also been observed. The biomass to be obtained from these microalgae poses critical challenges to human health, especially if it is to be used as a foodstuff and food supplement (Ahmad et al., 2021). In space applications, this will lead to both the disruption of the microalgal system and to a contaminated food supplement. The fact that the habitat in a space station consists of a small, closed environment, used for multiple purposes, and that there is no precipitation due to microgravity, means that there is a high potential for cross-contamination from chemical and biological sources (Niederwieser et al., 2018b). In a highly controlled environment such as the ISS, sterilization can be easily applied, as it will be advantageous to be able to control the inflow of microalgae into the system when growing microalgae in PBRs (Revellame et al., 2021).

Bioremediation studies involving microalgae have shown that these are tolerant to various organic pollutants and can use them for cell metabolism (Singh et al., 2017b). Microalgae can also be expected to display these typical features in a space habitat. Hydrogen-based compounds such as hydrogen chloride, molecular hydrogen and hydrazine can be found at lethal levels for microalgae in the form of chemical pollutants in spaceships. However, some microalgae species are known to be capable of tolerating these (Lee et al., 2000).

The most critical and greatest challenge for microalgae cultivation in space missions is the design of PBRs. These designs can vary significantly depending on conditions such as microgravity conditions on the ISS in LEO orbit, space travel within space missions, or the partial gravity of the surfaces of other planets. Accordingly, the PBR to be designed should be based on fluid dynamics in order to facilitate homogeneous mixing (Detrell, 2021). Since the reactor design will also affect the microalgae harvesting process, it will also need to perform processes such as centrifugation, filtration and flocculation (Revellame et al., 2021).

Considerable research is currently taking place into the design and operation of PBRs that will create a controlled life support system capable of providing food supplements and oxygen production for long-term space exploration. A PBR was designed and manufactured by Ai et al. (2008) for a controlled ecological life support system in which *Spirulina platensis* cultures would be grown. The reactor consists of nine systems: lighting, carbon dioxide feeding, oxygen removal, biomass collection, nutrient regeneration, parameter measurement and control, a heat exchanger and a culture cabinet. When the productivity of microalgae and the performance of the photo-bioreactor were evaluated the authors concluded that the principle of supplying CO_2 to the photo-bioreactor and removing O_2 from the culture medium met the demands in space conditions.

Numerous studies of biological life support systems have been carried out by major space agencies such as ROSKOSMOS, NASA, JAXA and ESA over the last 50 years, and significant advances have been registered in recycling technologies. One of the largest of these studies is the MELiSSA (micro-ecological life support system) project, conducted by the European Space Agency (ESA) for more than 30 years in the field of examining regenerative life support systems for long-term space missions. An aquatic ecosystem was planned in this project, which consisted of five phases (Lasseur et al., 2010). An efficient PBR unit is one of the main tasks of R&D in the MELiSSA project. Oxygen production from carbon dioxide within the MELiSSA Cycle is accomplished by photosynthetic chambers with net condensation via photobioreactors in order to obtain potentially edible biomass. *S. platensis* (*Arthrospira platensis*), a Cyanobacterium, was selected for use in the studies. This was due to its light energy conversion efficiency, its ability to grow in a high pH environment that reduces contamination, its high nutritional value and its ability to adapt to a wide variety of culture conditions, including space radiation. It showed that sufficent light energy flow is needed for metabolic needs and the main growth rate of Arthrospira in the reactor chamber. A representative version of the process, known as ARTEMISS, has been installed on the ISS. This enabled the oxygen production and nutritional supplement properties of the mechanism to be tested during the space flight (MELiSSA, 2022).

6. Results

With the beginning of the space age, intensive studies have started on organic materials that will meet the needs of astronauts in space. Although microalgae cultivation is seen as the first step, time is needed for this to become profitable. However, significant research has been done on this subject, and is still ongoing. Extreme conditions such as microgravity, vacuum, and extreme temperatures have not been observed to have significant effects on the growth of microalgae. The most promising studies on this subject are those on developing bioregenerative support systems. The aim of the next long-term space trips to be made by humans is to develop self-sufficient strategies rather than sending the resources to support human life from Earth.

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CHAPTER III

THERMAL ENERGY STORAGE SYSTEMS

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1. Introduction

Thermal energy storage (TES) is an energy storage technology used for the storage and subsequent utilization of heat energy. This technology is employed to balance the imbalances between energy demand and supply, enhance energy efficiency, and manage the variable nature of renewable energy sources. When energy is inaccessible or during energy interruptions, the required amount of energy can be supplied from energy storage systems. A thermal energy storage system operates by storing heat energy and subsequently converting it back into either electrical energy or heat Energy (Bayram & Orhon, 2020). These systems typically utilize materials that operate at high temperatures. Heat energy is stored in a thermal storage medium and can be later converted and utilized as electrical energy or heat energy. It is evident that thermal energy storage systems play a significant role among the energy storage solutions actively used today. These systems offer an effective solution to balance energy demand and supply, manage the variable nature of renewable energy sources, and enhance energy efficiency. However, further research and development efforts are necessary to advance the technology and minimize environmental impacts. This study provides a general overview of thermal energy systems.

2. Historical Development of Thermal Energy Storage Systems

Thermal energy storage, as a crucial component of energy storage technologies, has a long history dating back to ancient times. Throughout history, various methods have been developed to meet the need for energy storage. The origins of thermal energy storage can be traced back to ancient times when the first methods for storing and utilizing heat were developed. During the ancient Roman era, a heating system called the Hypocaust was employed. This system involved circulating heated air through stone walls and beneath the floor to store and distribute heat (Başaran, 1997). Similarly, in ancient China, different methods were used for heat storage. For instance, solar-heated water storage tanks were utilized to store heat energy and utilize it during nights or cloudy days.

The modern history of thermal energy storage technology began in the 19th century. In the early 1800s, Scottish inventor Robert Stirling invented the Stirling engine, which is named after him. The Stirling engine contains a mechanism that converts heat into thermal energy (Yaman & Erol, 2022). This engine also has the potential for thermal energy storage. However, due to insufficient interest in energy storage technologies at that time, the storage potential of the Stirling engine could not be fully realized. In the early 20th century, more research on thermal energy storage commenced. In 1903, Swedish inventor Gustaf Dalén developed a device called the Dalén light, which used acetylene gas to store heat energy. This light stored energy throughout the day and provided illumination during the night (Ashworth, 2017). Starting from the 1950s, there was increased focus and development on thermal energy storage systems. In the 1970s, solar thermal storage systems gained attention, and many thermal storage systems were designed during this period. Many of these systems utilized high-temperature salts and molten salts to store thermal energy (Koçak & Paksoy, 2020; Ali et al., 2021).

Currently, thermal energy storage technologies are advancing rapidly and being employed in various fields. Particularly with the increasing utilization of renewable energy sources, thermal energy storage systems have become an important tool to manage the variable nature of sources such as solar and geothermal energy and balance energy demand and supply.

3. Working Principle of Thermal Energy Storage Systems

Thermal energy storage (TES) systems are designed to store energy for later use. These systems utilize materials that operate at high temperatures and thermal storage mediums to store thermal energy, which can be later retrieved as either electrical energy or heat energy.

The fundamental working principle of a thermal energy storage system involves the storage and retrieval of thermal energy, typically through the stages of charging, storage, and discharging. The charging stage involves transferring thermal energy into the storage medium. During this stage, the energy storage medium is heated to high temperatures, which is often achieved through external sources such as solar energy, geothermal energy, combustion processes, or electrical energy. The heated storage medium facilitates the conversion of heat into thermal energy, which is then stored. In the storage stage, the thermal energy obtained from the previous stage is stored within the thermal storage medium. The storage medium is designed with an adiabatic structure that minimizes heat loss, allowing the stored energy to be preserved for extended periods. The storage medium must be well-insulated and isolated to minimize the loss of thermal energy. The discharging stage involves the retrieval of the stored energy for utilization. When needed, the thermal energy within the storage medium is released and converted into a different form for use. This discharging process is typically achieved by converting the thermal energy into either electrical energy or heat energy (Kocaman, 2021).

Thermal energy storage systems are generally based on three main principles: latent heat storage, thermochemical storage, and sensible heat storage. Latent heat storage involves storing the energy released during phase change. When a material undergoes a phase change from liquid to solid, a specific amount of energy is released. This released energy can be stored, serving as an example of latent heat storage (Baytorun et al., 2018). Thermochemical storage involves storing energy through chemical reactions. These reactions take place within a storage medium designed for energy storage, and the stored energy can be retrieved when the reactions are reversed (Yılmazoğlu, 2010). Sensible heat storage is used when temperature changes within a material are stored. The material stores energy at high temperatures and releases the stored energy to its surroundings at lower temperatures (Yılmazoğlu, 2010).

A thermal energy storage system operates through the integration of several components, including the thermal storage medium, heat transfer medium, heat exchangers, storage tanks, and control systems. The thermal storage medium is the primary material responsible for energy storage. The heat transfer medium facilitates the transfer of heat between the storage medium and the medium where energy conversion occurs. Heat exchangers enable the release of energy from the storage medium to the surrounding environment. Storage tanks house the energy storage medium. Control systems regulate the processes of storage and retrieval. Overall, thermal energy storage systems play a crucial role in balancing energy demand and supply, managing the variable nature of renewable energy sources, and improving energy efficiency. Further research and development efforts are necessary to advance the technology and minimize environmental impacts associated with thermal energy storage systems.

4. Advantages and Disadvantages of Thermal Energy Storage Systems

Thermal energy storage systems offer several advantages and provide an effective solution for energy storage. However, these systems also come with certain disadvantages. With the advancement and improvement of technology, it is expected that thermal energy storage systems will be further developed and widely adopted.

Thermal energy storage systems generally offer high efficiency. In a well-designed system, the energy loss during the storage and retrieval of thermal energy is minimal, allowing for more efficient utilization of energy. Compared to other energy storage technologies, thermal energy storage systems typically have high storage capacity, enabling large amounts of energy to be stored for extended periods. Thermal energy storage systems are usually long-lasting. When used correctly and maintained regularly, these systems can operate smoothly for many years, providing a long-term energy storage solution. Additionally, thermal energy storage systems can withstand prolonged operating hours due to the stability and durability of the storage medium, reducing the need for frequent maintenance. Many thermal energy storage systems are considered environmentally friendly. Particularly when used in conjunction with renewable energy sources, they contribute to the reduction of carbon dioxide emissions and promote sustainable energy use. These are among the advantages of thermal energy storage systems (Okazaki, 2020).

However, thermal energy storage systems have limited storage capacity, which can present challenges when large-scale energy storage is required. The volume and thermal properties of the storage medium are factors that determine the amount of energy stored. During the thermal energy storage process, some energy losses can occur due to heat transfer as the storage medium heats up or cools down, which can affect the overall efficiency of the system. Thermal energy storage systems can be expensive, especially for large-scale storage projects where the cost of the storage medium and installation process becomes a significant factor. Nevertheless, with technological advancements, costs are decreasing, making these systems more accessible. Additionally, the environmental impacts of thermal energy storage systems need to be considered. Some storage mediums used in these systems can have environmental effects. Therefore, it is important to design and operate the systems while taking into account their environmental impact. These are among the disadvantages of thermal energy storage systems.

5. Types of Thermal Energy Storage Systems

Thermal energy storage systems can be categorized into different types based on the methods and technologies used for storing and retrieving thermal energy. These systems offer various approaches for the storage and recovery of thermal energy.

Sensible Heat Storage Systems: Sensible heat refers to the amount of heat required to change the temperature of a substance without undergoing a phase change. Sensible heat storage systems are the most commonly preferred systems among thermal energy storage options. This is mainly due to the use of easily accessible materials such as ceramics, air, sand, and bricks. Sensible heat storage methods have their own advantages and disadvantages. For instance, a small storage volume is a disadvantage, while the availability of multiple storage options is an advantage (Konuklu et al., 2015).

Thermal Energy Storage at Varying Temperatures: Temperature storage systems store thermal energy based on temperature differences. These systems utilize temperature differentials to store and release energy. They can convert the stored energy into electrical energy by utilizing temperature variations.

Chemical Storage Systems: Chemical storage systems store thermal energy through chemical reactions. In these systems, a chemical reaction facilitates the storage and retrieval of energy. The chemical compounds used in such systems play a crucial role in storing and releasing energy (Zeinelabdein et al., 2018).

Latent Heat Storage Systems: Latent heat refers to the heat absorbed or released by a system at a constant temperature during a phase transition. It is the process where the system's temperature remains constant while the state of matter changes. The heat released during this phase change can be stored (Mishra et al., 2015). Latent heat storage systems have a higher capacity for storing latent heat compared to sensible heat (Günerhan, 2004). Therefore, latent heat storage systems can be considered more efficient. The aforementioned systems represent some common types of thermal energy storage systems. Each system type offers different advantages and disadvantages and may vary in terms of application areas. As technology advances, it is expected that newer and more efficient thermal energy storage systems will emerge.

6. Components of Thermal Energy Storage Systems

Thermal energy storage systems consist of various components that enable the storage, retrieval, conservation, and utilization of energy. These components play a crucial role in ensuring the efficient operation of the system. The key components of thermal energy storage systems include the storage medium, heat exchangers, heat sources, heat pumps, and control systems.

The storage medium is a central component where thermal energy is stored and retrieved. This medium should possess characteristics such as high temperature resistance and thermal conductivity. Commonly used materials for the storage medium include steam, salt solutions, thermal oils, or hydrogen. These materials can absorb and retain thermal energy. The storage medium should be insulated to minimize energy loss during the energy storage process.

Heat exchangers facilitate the transfer of temperature during the storage and retrieval process of thermal energy. They work in conjunction with the storage medium to facilitate energy storage and recovery. Typically, these components utilize pipelines or plates to facilitate energy transfer. Heat exchangers need to be optimized for high efficiency to enable efficient thermal energy storage and retrieval.

Heat sources are components that provide energy to thermal energy storage systems. Different sources such as solar energy, geothermal energy, combustion processes, or electrical energy can heat the storage medium to high temperatures. These sources are necessary for the operation of thermal energy storage systems and fulfill the energy demands of the systems.

Heat pumps are components that enable temperature transfer in thermal energy storage systems. They transfer energy efficiently between the storage medium and the heat sources during the storage or retrieval process. Heat pumps facilitate the transfer of thermal energy within the desired temperature ranges to the storage medium or the heat sources during the recovery process.

Control systems are components that manage and regulate the operation of thermal energy storage systems. These systems monitor the temperature and pressure levels of the storage medium, regulate energy transfer, and ensure the efficient operation of the system. Control systems work automatically to maintain the safe and stable operation of thermal energy storage systems and intervene when necessary (Ma et al., 2022).

These components form the essential building blocks of thermal energy storage systems. Together, they enable the storage, preservation, and retrieval of energy. Proper design and functionality of each component contribute to the effective and efficient operation of thermal energy storage systems.

7. Capacity Range in Thermal Energy Storage Systems

The capacity range of thermal energy storage systems refers to the amount of energy that these systems can store. This range can vary depending on different thermal energy storage technologies and applications. The capacity range of thermal energy storage systems is typically expressed in units of megawatt-hours (MWh) or gigawatt-hours (GWh). However, the capacity range can vary depending on the size, design, and intended application of the system. In small-scale applications, the capacity can be around a few MWh, while in large-scale energy storage projects, it can reach several GWh. The capacity of thermal energy storage systems is related to their ability to balance fluctuations in energy demand and resources. These systems can store excess energy when the demand is low and utilize it during energy conversion and storage processes. When the demand is high, the stored energy can be retrieved to meet the energy demand. In this way, thermal energy storage systems enhance the efficiency of the energy system by balancing energy supply and demand. The capacity range of thermal energy storage systems is directly linked to the volume and thermal properties of the storage medium. For example, liquid salt storage systems can typically have larger capacities because they provide a high-density storage medium. Such systems are used in large-scale energy storage projects. Other thermal storage technologies may be limited to smaller capacities. Additionally, the capacity of thermal energy storage systems is influenced by the storage duration. The storage duration determines how long the energy can be preserved in the storage medium. As the storage duration increases, the system can store more energy. The storage duration can vary depending on the application purpose and requirements. For instance, a thermal energy storage system operating with solar energy may require a longer storage duration to store the energy generated throughout the day (Rolka et al., 2021).

8. Environmental Issues in Thermal Energy Storage Systems

The components and materials used in thermal energy storage systems can have environmental impacts. For example, some chemicals used in storage media can be environmentally harmful. Therefore, environmental considerations should be taken into account during the material selection stage, favoring the use of sustainable and eco-friendly materials whenever possible. The energy sources of thermal energy storage systems can contribute to environmental impacts and climate change. For instance, energy sources based on fossil fuels can increase greenhouse gas emissions. Hence, the use of renewable energy sources is crucial to enhance the environmental sustainability of thermal energy storage systems (Singh et al., 2022). Proper management of waste generated during the operation phase of these systems is essential. The waste generated during the replacement of storage media or renewal of system components should be managed and recycled correctly. Additionally, appropriate disposal or recycling methods should be applied when the systems reach the end of their life. Some thermal energy storage systems may utilize water as a storage medium or for cooling purposes. This can have implications on water consumption and environmental impacts related to water recycling. Therefore, sustainable water resource management and water conservation measures should be considered to reduce the environmental effects of thermal energy storage systems (Olabi et al., 2021). Measures should be taken to reduce energy consumption and environmental impacts during the operation and maintenance stages of thermal energy storage systems. Efficient operation strategies and regular maintenance ensure the effective use of energy resources and make the systems more environmentally friendly. These issues represent areas that need to be considered in terms of the environmental sustainability of thermal energy storage systems. Therefore, the design, operation, and waste management processes of these systems should be carried out based on sensitivity to environmental impacts and sustainability principles. In this way, thermal energy storage systems can minimize their negative effects on the environment while fulfilling energy storage needs.

9. Usage of Thermal Energy Storage Systems Worldwide

Thermal energy storage systems are being used as part of energy storage projects in many countries. With the increasing use of renewable energy sources, the importance of these systems has grown even further. Thermal energy storage systems have significant potential for the efficient utilization of fluctuating and time-varying energy sources such as wind and solar energy. Many countries utilize thermal energy storage systems to manage energy demand and enhance energy security. For instance, countries like Germany, the United Kingdom, the United States, China, and Australia incorporate thermal energy storage systems as central components of large-scale energy storage projects. These projects are used to stabilize the power grid in regions with fluctuating energy production and to utilize energy more efficiently. In some countries, thermal energy storage systems are also used for meeting heating and cooling needs. For example, energy savings can be achieved by employing thermal energy storage technologies for building heating and cooling systems. These systems store heat, reducing fluctuations in energy demand and offering a more sustainable heating/cooling solution. The utilization of thermal energy storage systems is increasing in parallel with advancements in energy storage technologies. New materials, more efficient storage mediums, and advanced control systems enhance the performance and utilization of thermal energy storage systems. Furthermore, cost reductions and government policy support contribute to the adoption of thermal energy storage systems (IREA, 2020). The usage of thermal energy storage systems worldwide is closely linked to efforts to achieve energy transformation and sustainable energy goals. These systems serve as crucial tools for enabling the more effective utilization of renewable energy sources, ensuring energy stability, and reducing the reliance on fossil fuels.

10. Usage of Thermal Energy Storage Systems in Turkey

Turkey is a country rich in the diversity and potential of renewable energy sources. Renewable energy sources such as wind energy, solar energy, biodiesel, bioethanol, biomass, hydroelectric power, and geothermal energy play a significant role in Turkey's energy supply. Due to the fluctuations and variability of these sources, thermal energy storage systems offer an ideal solution for balancing energy and ensuring stability. Thermal energy storage projects in Turkey are used in various areas such as managing energy demand, improving energy efficiency, and stabilizing the power grid. Particularly in regions where fluctuating energy sources like solar and wind energy are utilized, thermal energy storage systems play a crucial role in balancing energy production fluctuations (Özdoğan, 2010). These systems store excess energy during periods of low demand and enable its efficient utilization. The usage of thermal energy storage systems in Turkey is supported by the steps taken by the government in the fields of renewable energy and energy storage. Projects and incentives implemented by the Ministry of Energy and Natural Resources encourage the development of thermal energy storage systems. Research and development activities and pilot projects focused on energy storage technologies contribute to the increased utilization of thermal energy storage systems. One of the advantages of using thermal energy storage systems in

Turkey is the enhancement of energy security. Indigenous energy production and storage based on renewable energy sources enable Turkey to pursue a more independent and sustainable energy path. Additionally, thermal energy storage systems enhance energy efficiency and facilitate the more effective utilization of energy resources. However, the utilization of thermal energy storage systems in Turkey is still in the developmental stage. Technological advancements and cost reductions will promote the wider adoption of thermal energy storage systems. Nevertheless, Turkey's potential in renewable energy-based production and storage indicates that thermal energy storage systems will have a more widespread usage in the future.

11. Conclusion

Thermal energy storage systems are advanced storage solutions that play a significant role in the energy sector and are critical in meeting future energy demands. These systems offer significant advantages in balancing the fluctuations of renewable energy sources, managing energy demand, ensuring grid stability, and enhancing energy efficiency. This study has addressed various aspects of thermal energy storage systems, including general information, working principles, history, advantages and disadvantages, types, components, capacity range, and environmental issues. With advancements in energy storage technologies, thermal energy storage systems are increasingly being used and developed. The operation principle of these systems is based on the storage and release of thermal energy among different components, enabling flexible energy supply according to energy demand. Different types of systems are available, including simple heat storage systems, thermal oil storage systems, thermal salt storage systems, and thermal concrete storage systems.

Thermal energy storage systems offer numerous advantages, such as ensuring energy supply stability, increasing energy efficiency, supporting the effective utilization of renewable energy sources, managing energy demand, enhancing energy security, reducing carbon footprint, and promoting sustainability. However, they also have some disadvantages, including high costs, space requirements, and certain environmental impacts. The utilization of thermal energy storage systems is increasing worldwide and in Turkey. Particularly, with the growth of renewable energy sources, thermal energy storage systems play a crucial role in meeting energy storage needs. Government support, technological advancements, and cost reductions encourage the widespread adoption of thermal energy storage systems.

In conclusion, thermal energy storage systems have great potential in the energy sector and offer an effective solution for meeting energy storage needs. However, further research and development, technological advancements, and cost reductions are necessary for continued progress. The utilization of thermal energy storage systems is also increasing in Turkey, contributing to the steps taken towards a sustainable future in the energy sector. These systems are of significant importance in ensuring energy stability, increasing energy efficiency, and supporting the more effective utilization of renewable energy sources.

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CHAPTER IV

NANO ENERGY

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1. Introduction

Nanotechnology is a new advanced technological science that tries to explain today's events in nanoscale. Nanotechnology is the science of controlling the structure of matter and material relationships at the advanced atomic and molecular level. In general, for materials with a size of 100 nm and smaller, and for new technological devices developed. For example, photosynthesis is an event that takes place at the nano nanoscale (≤100 nm) rather than an electrochemical event. In the electrochemical cell, photosynthesis takes place and turns into light energy and chemical energy. The original carbon-based fuels in the existing structure constitute the most important event in the production of other fuels. Scientific fields such as nanoelectronics, nanomechanics, nanophotonics and nanoionics have only recently been introduced to provide a scientific basis within the field of nanotechnology. Nanoscience and nanotechnology cannot be defined with exact description, but can be defined in terms of understanding, control, and functionalization of materials at the atomic level, at a scale of 1 to 100 nanometers (nm). Nanoscience is an 'interdisciplinary science' i.e. chemistry, physics etc. It includes concepts from more than one discipline, such as. Nanotechnology is science, engineering and technology at the nanoscale, which is about 1 to 100 nm. The most well-known expression of nanoscience is the science that explains the properties of materials in atomic, molecular and macromolecular dimensions and states that these properties are different from those in larger dimensions (The Royal Society, 2004) Nanoscience is a multidisciplinary science. Nanoscience, in short, is the science and field of Nanotechnology, the characterization, production and application of atoms and molecules, analytical devices and designed structures with appropriate setups by controlling shape, size and nanometric dimension.

The father of nanotechnology, Physicist Richard Feynman, Nanotechnology science and the ideas, applications and concepts behind nanotechnology science, long before the formation of nanotechnology terminology, on December 29, 1959 at the California Institute of Technology, at the American Physical Society meeting, physicist Richard Feynman's "Below It started with his speech titled "There's a Room" and was first used as a term at that time. In his conference speech, Feynman described a delicate process in which scientists manipulate and control atoms and the molecules they form (Acar, S., 2022).

Table 1. Sizes of nano-particles, wave length of visible lights, and atoms and molecules

Physical examples	Size (m)
Nano particles	$3\text{-}5x10^{-9}$
Visible lights	$4\text{-}7x10^{-7}$
Atoms and molecules	$1\text{-}2x10^{-10}$
X-rays	$1x10^{-8}\text{-}1x10^{-12}$
Gamma rays	$1x10^{-12}\text{-}1x10^{-13}$

A nanostructured advanced material is a one-dimensional object in the nanoband (1 nm-100 nm band). Nanoadvanced materials are also categorized according to their level as given in Table 2.

Table 2. Nanomaterials are classified according to their dimensions

Dimension of nanomaterial	Typical example
All three dimensions < 100 nm	Nanoparticles, quantum dots, nanoshells, nanorings, microcapsules
Two dimensions < 100 nm	Nanotubes, fibres, nanowires
One dimension < 100 nm	Thin films, layers and coatings

The field of nanotechnology facilitates this by manipulating the smallest building blocks of all atoms of all materials in the structural dimension, again in the smallest dimension. By organizing and renewing this scope, science can design new and advanced products with new chemical, planetary and physical structures.The results of nanotechnology studies have features that have never been seen before, allowing us to reach conclusions (Acar, S., 2022; Demirbas, A., 2011b).

The term nanotechnology (commonly abbreviated as "nanotech") is the process of manipulating the structure of matter at the atomic or molecular scale. In general, nanotechnology deals with the application and development of at least one-dimensional materials, devices, or other material structures in the 3x10-9 to 5x10-9 nanometer band. Quantum mechanics interactions are important at this quantum field level (Acar, S., 2022).

In general, materials can show different properties at the nanoscale (≤100nm) due to quantum structure dynamics. Nanotechnology has the potential to be applied in the fields of medicine, electronics and energy production. Table 3 shows the molecular size of nanoparticle structures, visible light and atoms, as well as structures. To put this structure in another way, the comparative size of a nanometer to a meter is directly proportional to the comparison of a marble to the size of the earth, or to put it another way: A nanometer is the amount of time it takes the average man to bring the shaver to his face, and his beard grows. We can also say.

Table 3. Size of nano particles, visible lights and atoms and molecules.

Visible lights	Atoms and molecules	Nano particles
$4\text{-}7x10^{-5}$ cm	$1\text{-}2x10^{-8}$ cm	$3\text{-}5x10^{-7}$ cm

The term nanotechnology (often shortened to "nanotech") can be viewed as the process of manipulating the dimensional aggregate of material at the atomic and advanced molecular scales. In fact, the science of nanotechnology encompasses the work of developing materials, devices, or other structural constructs with at least one dimension between 1 and 100 nanometers (nm). Mechanically, the effects of quantum are important in the quantum realm scale of these structures.

2. Geometric Energy

There is an indirect relationship between the symmetry of an object and the energy field or linearly the energy depends on the geometry of the object. Energy is actually a geometric conceptual structure. Geometric factor for energy differences manager. It can also be said that the energy potential consists of geometric differences. Also, energy is inversely proportional to volume. As the wavelength of an electromagnetic wave decreases, its energy increases. This phenomenon is called the frequency factor. Therefore, the frequency of a wave is indirectly proportional to the radiated energy.

The geometry of energy can actually be better expressed on the smallest scale, the nanometer scale. It is more effective in nanometric dimensions due to geometric structural interaction. Therefore, it is affected by precious metals with nano size structures that do not interact chemically.

3. Global Energy Sources and Present Energy Situation

Today, the universe in general faces three sensitive problems: (1) costly fuel prices, (2) climate change indicators, and (3) air pollution emission values. Scientists suggest that current oil and gas reserves will only last for a few more decades. It is well known for logistics and is almost on fossil fuels, especially petroleum-based fuels such as gasoline, diesel, LNG and CNG. Petroleum-based fuels are limited field reserves clustered in certain areas of the world. The constant and rapid increase in oil prices, the limited use of fossil fuels, and the rapid increase in concerns about environmental interactions, especially greenhouse gas emissions, necessitate the search for new and renewable energy sources and alternative systems (Sigar, C.P., et al., 2009; Balat, 2009). M., 2009; Balat M., 2011; Demirbas, A., 2011a; Demirbas, A., 2011b; Demirbaş, T., 2011b)

Oil reserves in existing fields are limited resources. Many more studies reveal the history of the global peak in fuel production from oil reserves at the fields between 1996 and 2035. Biomass energy technologies used for waste or plant matter to produce energy with a lower level of greenhouse gas emissions than fossil fuel sources (Sheehan, J., 1998).

4. Nano Energy Facilities

Photosynthesis is an electrochemical process used via plants and other organisms to capture the sun's energy to split off water's hydrogen from oxygen. Hydrogen combined with carbon dioxide (absorbed from air/water) to form glucose and release oxygen to atmosphere. All living cells in turn use fuels produced from glucose and oxidize the hydrogen and carbon to release the sun's energy and reform water and carbon dioxide in the reaction (cellular respiration):

$$CO_2 + H_2O \xrightarrow[\textbf{Electrochemical Cell}]{\textbf{Sunlight}} CH_2O + O_2$$

Fig. 1. Cellular respiration

Table 4. Global renewable energy scenario by 2040

	2001	**2010**	**2020**	**2030**	**2040**
Total consumption (Million ton oil equivalent)	10038	10549	11425	12352	13310
Biomass	1080	1313	1791	2483	3271
Large hydro	22.7	266	309	341	358
Geothermal	43.2	86	186	333	493
Small hydro	9.5	19	49	106	189
Wind	4.7	44	266	542	688
Solar thermal	4.1	15	66	244	480
Photovoltaic	0.2	2	24	221	784
Solar thermal electricity	0.1	0.4	3	16	68
Marine (tidal/wave/ocean)	0.05	0.1	0.4	3	20
Total renewable energy sources	1365.5	1745.5	2694.4	4289	6351
Renewable energy sources contribution (%)	13.6	16.6	23.6	34.7	47.7

The energy sector, which is the biggest and most challenging strategic issue we face in the world, has the potential to eliminate some problems with the developments in the field of nanotechnology; Fossil fuels are becoming cleaner, safer and cheaper to produce for a more environmentally friendly and environmentally friendly form than they are now. As an alternative, renewable sources are cheaper to generate electricity than others and easier to implement. In addition, Nuclear energy sources, Uranium-based reactors, recycling processes of radioactive by-products will be safer, smaller and more cost-effective. Significantly, nanostructured material and new types laser devices developed allowed to extract nuclear energy without resorting to brute-force methods and radioactive by products (Sweeney AE., 2008).

5. Conclusion

The potential benefits of nanotechnology as a direct participant for advanced Space programs to be considered going forward may include:

— Nanostructured devices for advanced monitoring of drive system structure and efficient control systems.

— To make spacecraft resistant to strength, lighter, stronger and radiation resistant.

—Advanced Computer-controlled systems equipped with Artificial Intelligence and nanorobotics.

— Advanced improvements to clothing for space travel or research.

— Possibility to build Space elevators and large space colony structures, more useful in space base projects.

— Developments in space telescopes, one of the space imaging systems, in terms of taking images in space and examining advanced universes.

Summary of the benefits of advanced nanotechnology, which can also contribute to the field of nuclear energy (Shrair J. S., 2010):

— Micro-size or advanced nano-chemical processing as a reprocessing technology to add to nuclear materials and systems.

— Advanced material nanoparticles with high surface area for catalysis or ion exchange steps.

— Strengthening the international safeguards system with new detection devices to cover both declared and undeclared activities.

— Self-cleaning surfaces for decontamination of plants.

— Process steps for making advanced materials such as nanomaterials and indirectly energy conversion devices.

It is capable of achieving high and fast conversion efficiency of up to 99.9%.

— Advanced nanostructured/nanocomposite materials for advanced nuclear fuels or as new waste forms thereof.

— “Lab on a chip” diagnostic technologies for on-line process monitoring and control in a wide range of operations.

— Realization of new process steps and new dimensional approaches with the ability to develop new processes related to alternative fusion step processes energy.

— To be able to design nano-scale nuclear power devices with similar capabilities such as nano-nuclear batteries to be designed as advanced materials.

— As a result of the studies, an effective and more useful inexpensive method for the recycling of nuclear waste.

— Possibilities of building Nano-Micro-Reactors to produce commercial fusion power.

— Realization of nuclear fusion at lower temperatures with nano-sized nanostructured materials to be obtained as advanced materials.

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CHAPTER V

TREATMENT OF WASTEWATER CONTAINING AZO DYES BY COMBINED PROCESSES

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1. Introduction

Azo dyes are an essential type of dye widely used in textile, leather, food, cosmetics, and paper products because they are economical, easy to synthesize, have high hardness, and offer a wide colour range. Approximately one million tons of azo dyes are estimated to be produced, and more than 2000 azo dyes with different structural properties are used worldwide (Stolz, 2001; Vijaykumar et al., 2007). Azo dyes are characterized by containing one or more (-N=N-) groups attached to aromatic rings, and their colour is related to the azo bond and chromophores (Zhang et al., 2005; Lodha & Chuaudhari, 2007; Aleboyeh et al., 2009; Rawat et al., 2018). The classification of azo dyes has been depicted in Figure 1.

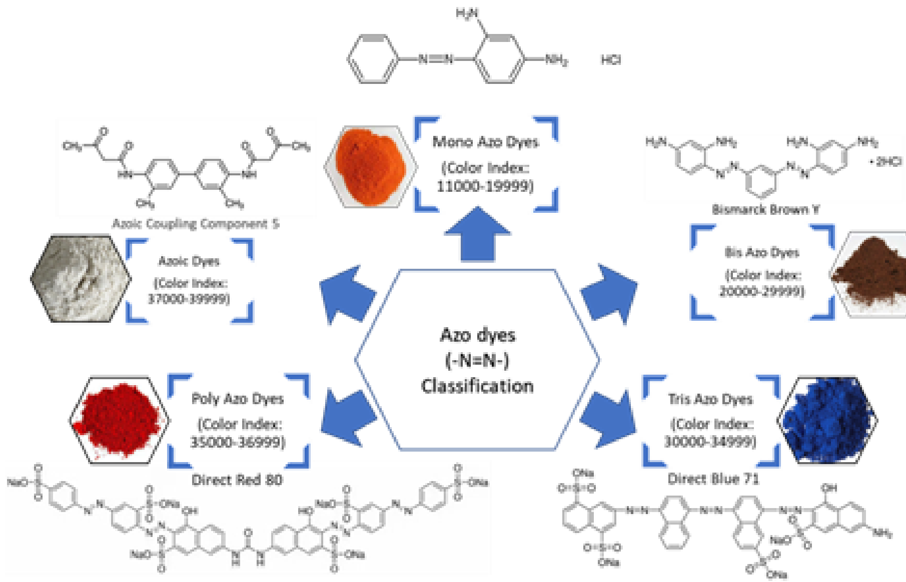

Figure 1. Classification of Azo Dyes

Most azo dyes are harmful to the environment, as azo dyes are resistant to degradation and some azo dyes produce toxic metabolites. Wastes generated from the paint industry are typically characterized by high levels of dye, suspended solids, biological oxygen demand (BOD), and chemical oxygen demand (COD). Wastewater with high COD content reduces the dissolved oxygen required for everyday life and makes wastewater treatment more complex, so it is essential to remove waste before disposal (Kulla et al., 1983; Chung & Stevens, 1993; Matthew et al., 1993; Weisburger, 2002; Dörtkol, 2014; Chung, 2016; Rawat et al., 2016). Improper treatment of these wastes can have direct or indirect impacts on various ecosystems, as illustrated in Figure 2. Therefore, urgent calls have been made to treat wastewater containing azo dyes or convert them into useful and safe products (Madhav et al., 2018; Jamee et al., 2019).

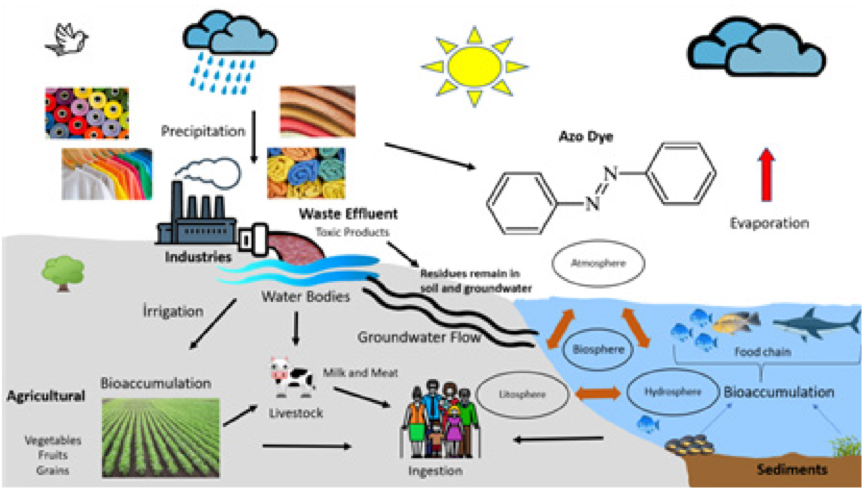

Figure 2. Direct and indirect impacts of azo dyes on several ecosystems

In recent years, a variety of chemical, physical, and biological treatment methods have been developed for the removal of wastewater containing azo dyes (Hao et al., 2000; Maier et al., 2004; Ravadelli et al., 2021). Integrated processes improve the biodegradation of wastewater containing azo dyes and reduce sludge production (Figure 3). However, these methods are not widely applied in the textile industries due to their high cost and disposal problems (Scott & Ollis, 1995; Scott & Ollis, 1997; Aravind et al., 2016; Chaturvedi et al., 2022).

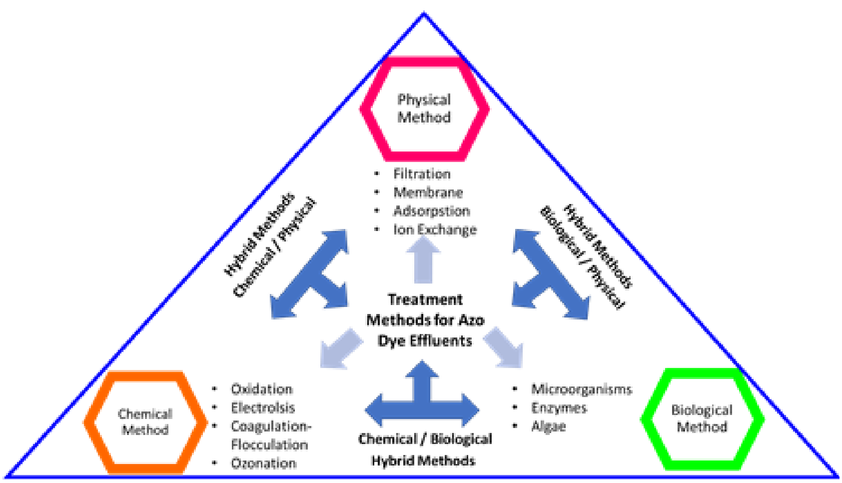

Figure 3. Various treatment methods used for the purification of azo dye effluents

Treatment of wastewater containing azo dye with integrated processes brings many advantages and disadvantages.

Advantages:

1. Integrated processes provide a more efficient treatment thanks to combining multiple processes instead of a single process (Chowdhury et al., 2018).
2. Integrated processes can be more effective for the removal of challenging contaminants such as azo dyes (El-Naas et al., 2011).
3. Integrated processes can reduce energy use in wastewater treatment plants and recover energy (Chen et al., 2017).
4. Some integrated processes can reduce sludge formation and the amount of solid waste generated from wastewater treatment (Su et al., 2016).

Disadvantages:

1. Integrated processes may require a higher investment cost (Aziz et al., 2004).
2. The design and operation of integrated processes can be more complex (Wang et al., 2010).
3. Some integrated processes may require further operational intervention (Dionysiou et al., 2018).
4. Integrated processes can increase staff training requirements in wastewater treatment plants (Ali et al., 2011).

This study aims to compile, classify, and critically evaluate the recent advancements in integrated treatment technologies utilized for the treatment of wastewater containing azo dyes. Additionally, this study intends to compare the advantages and disadvantages of these technology processes.

2. Physical and Biological Processes

The textile industry is known worldwide for its massive use of water and the generation of polluted waste. Therefore, in terms of reducing environmental pollution and sustainability, the treatment of the industry's wastewater is of great importance. Combining physical and biological processes is a method applied for the treatment of textile industry waste. Adsorption, chemical precipitation, and membrane separation are among the physical decolorization technologies that have been reported in the literature (Majewska-Nowak, 1992; Carriere et al., 1993; Cooper, 1993; Mckay, 1980; Piaskowski et al., 2018; Hashemi &

Kaykhaii, 2022). However, these techniques' high cost and disposal problems necessitated further investigation.

2.1. Azo Dye Removal via Adsorption Mechanisms

The inability of azo dye compounds to be degraded in biological treatment processes requires physical treatment to be an important step before biological treatment. In this way, the load of the processes that follow can be reduced, and legal discharge limits can be met.

In general, the adsorption mechanisms of azo dyes involve four distinct steps: bulk diffusion, film diffusion, pore diffusion or intraparticle diffusion, and chemical reaction. Of these steps, film diffusion, pore diffusion, and chemical reaction are considered the most critical. Previous studies have indicated that amine sites are the primary reactive groups for azo dyes, although hydroxyl groups may also contribute to adsorption.

Chemical adsorption can be achieved through various mechanisms, such as ion exchange and electrostatic attraction. The pH value is a crucial factor that influences the adsorption process. In contrast, chemisorption is a potent type of adsorption that does not involve the exchange of molecules but instead the exchange of electrons. When it comes to the adsorption of anionic dyes, chemisorption under acidic conditions is considered the primary mechanism. Figure 4 provides a brief explanation of this mechanism. In the presence of H^+ ions, the amino groups of chitosan become protonated, while the sulfonate groups in the anionic dye solution dissociate and convert into anionic dye ions. The adsorption process continues as a result of the electrostatic attraction between these two counter ions (Crini & Badot, 2008; Lu & Liu, 2010; Hashemi & Kaykhaii, 2022).

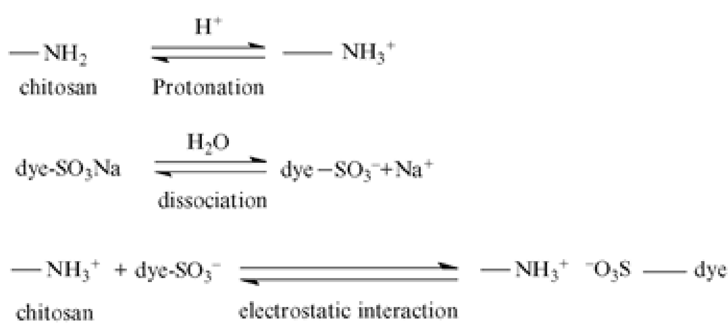

Figure 4. Mechanism of anionic dye adsorption by chitosan under high acidity conditions (Lu & Liu, 2010)

Research shows that integrated physical-biological processes provide high efficiency for the removal of azo-dye wastewater (Lu & Liu, 2010; Patel & Suresh, 2018). The adsorption process is considered the most effective physical process in the removal of azo dyes, and activated carbon, zeolite, clay and iron oxides are among the most widely used adsorbents (Lu & Liu, 2010; Tsekova & Tasheva, 2016).

2.2. Treatment of Azo Dye Wastewater through Physical-Biological Processes Combination

The treatment of wastewater containing azo dyes has been covered in many research papers using combined physical-biological processes. Sirianuntapiboon & Sansak (2008), combined granular activated carbon (GAC) and sequential batch reactor (SBR) systems to directly treat blue 201 and red 23 dyes in synthetic and raw textile wastewater. Ong et al. (2008), in a study investigating the combination of adsorption and biodegradation processes for the color removal potential of wastewater containing acid Orange 7, stated that 100% color removal was achieved by using a GAC-biofilm configured packed column system.

In the treatment of wastewater containing azo dyes, a combination of biological treatment processes and membrane technologies is frequently employed. Previous studies have utilised various membrane processes, such as microfiltration, ultrafiltration, and nanofiltration (NF), for treating biologically treated textile wastewater. These findings indicate that the treated water can be reused (Bes-Piá et al., 2003; Fersi et al., 2005). According to You et al. (2008), synthetic textile dyeing effluents can elevate the chemical oxygen demand (COD) and actual color removal of an anaerobic tank when combined with anaerobic-oxic membrane bioreactor and reverse osmosis (RO) processes. The study also showed that the RO unit was particularly effective in removing actual color. In addition, the RO unit can also further remove actual color. Successful application of anaerobic biodegradation of azo dyes has been observed in the decolorization of concentrations obtained from nanofiltration (NF) treatment of actual textile effluent (Żyłła et al., 2006; Gomes et al., 2007).

Dyestuffs that are resistant to aerobic degradation can be effectively removed through anaerobic degradation (Namal, 2017). Azo bonds in azo dyes are biodegradable under anaerobic conditions in the presence of external electron donors (Pandey et al., 2007). As a result of the biodegradation of azo bonds, most of them turn into aromatic amines that biodegrade easily (Bahadır, 2012). In this case, they cannot degrade further under anaerobic conditions (Işık & Sponza, 2008). Generally, the total biodegradation of azo dyes must occur in two stages. The first step is the anaerobic reduction of the azo bond, and the second step is the aerobic degradation of the aromatic amines formed (Libra et al., 2004). Paździor et al. (2009), reported that in the anaerobic biological azo dye reduction process, the aromatic amine released from the azo dye formed in the anaerobic phase is destroyed by nanofiltration of actual textile wastewater, and the aromatic amine is wholly degraded by aerobic oxidation applied after the anaerobic phase. The studies stated that it meets the water quality requirement by developing a combined process consisting of biological process (anoxic and aerobic) and bottom filter technology to treat printing and dyeing wastewater (Lu et al., 2009a; Lu et al., 2009b).

Nanofiltration and reverse osmosis processes are membrane technologies that show high efficiency in the removal of azo dyes (Nataraj et al., 2009). Also, in recent years, the use of bio composites for the removal of azo dyes has been explored. These bio-composites are formed by combining natural polymers and adsorbents and are considered an effective option for the adsorption and removal of azo dyes (Shah & Patel, 2018). Therefore, it is recommended to apply combined membrane-biological processes in the textile industry to close the water cycle and ensure environmentally sustainable development (El Defrawy & Shaalan, 2007). In this way, it will be possible to use NF-biological and RO-biological processes that enable water reuse and reduce freshwater consumption.

3. Treatment of Azo Dye-Containing Wastewater with Chemical-Biological Process Combinations

Wastewater treatment methods comprise chemical and biological processes. Reduction and oxidation are typically used in chemical treatments. Some examples of these processes include traditional chemical methods such as coagulation-flocculation, as well as advanced oxidation processes (AOP) like ozonation, Fenton oxidation, Fe^{2+}/H_2O_2, ultrasonic chemical oxidation, photocatalysis oxidation (UV/H_2O_2, UV/O_3, and $UV/O_3/H_2O_2$), H_2O_2, electrochemical oxidation, and irradiation oxidation. These techniques are utilized to treat wastewater generated from the textile industry that contains refractory waste (Ledakowicz et al., 2001; Rodriguez et al., 2002; Oller et al., 2011).

The treatment of textile wastewater often involves the use of biological processes. (Bidhendi et al., 2007). However, azo dyes are resistant to aerobic microbial degradation. One reason for this is that they are produced so that the colors do not fade to ensure the permanence of the azo dyestuff on the product (Mıdık, 2011). According to Willmott et al. (1998), the molecular weights of azo dyes are too large to pass through the biological cell membrane, which is another contributing factor. However, a study on the removal of color from textile wastewater containing azo, diazo, and reactive dyestuffs through microbial processes revealed that color removal could not be accomplished by pure bacterial cultures isolated from aerobic columns (Nigam et al., 1996). O'neill et al. (2000a) highlighted the insufficient performance of aerobic treatment in removing the color of textile wastewater containing azo dyestuffs, stating that only about 10% of reactive dyes such as azo dyestuffs in wastewater are adsorbed to aerobic biomass on average, while the rest passes through the activated sludge plant without any change.

Lucas et al. (2007), In a study investigating the decomposition of a reactive azo dye, which is widely used in the textile industry, by a chemical-biological process using Fenton reagent and yeast, they observed that the Fenton reagent increased the ability of the dye to break down. They also reported that yeast breaks down the dye particles into smaller molecules. They emphasized that using these two processes together provides a more effective paint removal method than when used alone. The results show that using Fenton reagent and yeast is a promising approach for disposing of industrial dyeing waste.

Fahmi et al. (2011), observed that the advanced oxidation process significantly reduced the color and COD levels, in a study investigating the properties of advanced oxidation processes and biological treatment methods in removing the color and COD level of azo dyes. However, they observed that biological treatment reduced color and COD levels. The results show that combining advanced oxidation process and biological treatment can be an effective method for removing azo dyes in aqueous solutions.

Yuan et al. (2023), observed that intermittent electric field stimulation accelerated the redox coupling reaction in a study using the intermittent electric field evoked redox coupling process (IERC) to increase azo dye biodegradation. In addition, it has been stated that azo dyes biodegrade faster and the efficiency of the biological treatment process increases. The results show that IERC can be an effective method for the biodegradation of azo dyes.

Studies in the literature show that chemical treatments alone may not be sufficient for the removal of azo dyes. For this reason, it should be supported by biological processes in combination with chemical processes. In recent years, numerous studies have suggested the integration of chemical processes with anaerobic or anoxic biological processes as a viable solution for the treatment of waste generated by the textile industry.

3.1. Removal of Azo Dyes Using an Oxidation Mechanism

The oxidation mechanism for removing azo dyes involves using oxidizing agents, such as ozone, hydrogen peroxide, and persulfate. These agents can break the azo bonds, which are the main structural feature of azo dyes. The oxidizing agent's attack typically breaks the azo bonds on the azo group's nitrogen atoms. Once the azo bond is broken, the dye molecule is transformed into smaller, more polar compounds that are easier to remove from the water. These compounds may be oxidized to form carbon dioxide, water, and other harmless by-products. The oxidation process can be carried out using different methods, including photocatalytic, electrochemical, and chemical oxidation. Photocatalytic oxidation uses a photocatalyst, such as titanium dioxide, to generate reactive oxygen species that can break down the azo dyes. Electrochemical oxidation uses an applied electric potential to generate oxidizing species at the electrode surface, which can then oxidize the azo dyes. Chemical oxidation involves the addition of an oxidizing agent to the wastewater to break down the azo dyes.

Among the oxidation mechanisms for removing azo dyes, Fenton oxidation is one of the oldest AOP successfully used because it is a relatively inexpensive and easy-to-use reagent. The Fenton system is based on the electron transfer of iron ions with H_2O_2 using hydrogen peroxide and iron ions as homogeneous catalysts. The added catalyst accelerates the decomposition of hydrogen peroxide and forms highly reactive hydroxyl radicals (·OH) according to the reaction scheme below (Rivas et al., 2001; Kušić et al., 2007; Sun et al., 2007; Farha, 2010).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + \cdot OH \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+ \qquad (2)$$

$$2H_2O_2 \rightarrow \cdot OH + HO_2\cdot + H_2O \qquad (3)$$

Hydrogen peroxide and iron ion mixture is an effective method for colour and COD removal of paint waste. The Fenton reaction is essential for degrading organic pollutants in wastewater treatment and other environmental applications. The formation of hydroxyl radicals is a critical step in this process.

Heterogeneous photocatalysis is a promising technique for the treatment of azo dyes within the realm of Advanced Oxidation Processes (AOPs). This method involves the activation of titanium dioxide (TiO_2) under UV irradiation (l < 390 nm), which leads to the production of highly reactive free radicals (·OH) from water or hydroxide ions. The free radicals can then react with the permanent components that are adsorbed on the surface of TiO_2 until complete mineralization is achieved (Mills & Hoffmann, 1993; Sillanpää et al., 2018; Armaković et al., 2022). Photocatalytic mechanisms of TiO_2 take place according to the following reaction scheme.

$$TiO_2 + hv \rightarrow TiO_2\,(e^- + \ h^+) \quad (4)$$

$$h^+ + HO^- \rightarrow \ \cdot OH \quad (5)$$

$$\cdot h^+ + HO_2 \rightarrow \ H^+ + \cdot OH \quad (6)$$

$$e^- + Ti^{4+} \rightarrow \ Ti^{3+} \quad (7)$$

$$TiO_2 \ + \ e^- + \ O_2 \rightarrow \ \cdot O_2^- + TiO_2 \quad (8)$$

$$2OH \cdot \rightarrow + H_2O_2 + \ O_2 \quad (9)$$

The photocatalytic mechanisms of TiO_2 and the biodegradation process of the OH radical oxidation of azo dyes share similarities. Figure 5 illustrates one of the proposed reaction mechanisms for the oxidation of azo dyes when reacting with the OH radical (Spadaro et al., 1994; Descorme, 2017).

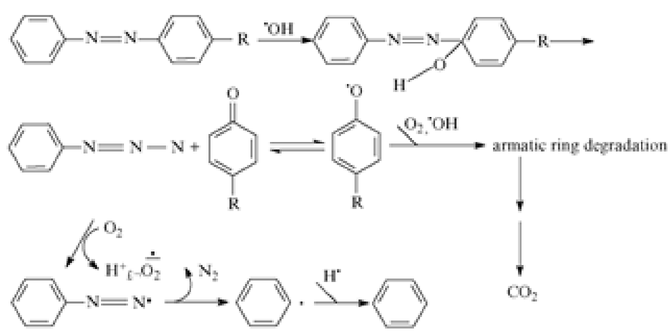

Figure 5. Reaction mechanism of oxidation of azo dyes reacted with (·OH) radical (Lu & Liu, 2010)

Ünal et al. (2019) investigated the efficiency of magnetite nanoparticles placed on a glass substrate for the removal of azo dyes through adsorption and Fenton oxidation. Their findings demonstrated that magnetite nanoparticles could effectively remove azo dyes by adsorbing and facilitating Fenton oxidation, indicating high efficiency in the removal of azo dyes. Thus, magnetite nanoparticles can be used as a promising material for efficient removal of azo dyes through adsorption and Fenton oxidation. In a separate study, Xia et al. (2020) examined various aspects of the electrochemical oxidation process, including parameter optimization, reaction mechanism, and toxicity assessment, by studying the electrochemical oxidation of Acid Orange 7 azo dye using a PbO_2 electrode. It was observed that the azo dye used was oxidized with a high removal efficiency, and the amount of waste produced in terms of toxicity was reduced. These results show that using PbO_2 electrodes can be a promising method for removing azo dyes and can be used in industrial applications. Tarkwa et al. (2019), have analyzed various aspects, including optimization of the process and mineralization mechanism, to remove Orange G azo dye by Photo-Fenton oxidation. They observed that Photo-Fenton oxidation could effectively oxidize Orange G azo dye and provide a high removal efficiency. The study shows that Photo-Fenton oxidation can be a promising option for the purification of azo dyes and can be used in industrial applications.

The results of these studies show that different oxidation mechanisms are effective in removing azo dyes. However, the effectiveness of the oxidation process depends on several factors, such as the chemical structure of the azo dye, pH, type and concentration of the oxidizing agent, processing temperature and processing time.

3.2. Combination of Chemical Coagulation-Biological Processes for Removal of Azo Dyes

The effectiveness of combined chemical coagulation-biological processes, which is a method in which reduction and biological treatment processes are combined, was investigated for the colour removal of non-biodegradable substances in textile dyeing wastewater. This method has come to the forefront as a new technique by showing higher efficiency and lower cost in experimental comparisons made at the laboratory scale with other reported combined chemical-biological methods (Ghoreishi & Haghighi, 2003).

Wang et al. (2021), the removal of Acid Red 14 (AR14) from synthetic wastewater was investigated using chemical coagulation with polyaluminum chloride and biological treatment with anaerobic-anoxic-oxy treatment. The results showed that the combined treatment effectively removed 96.2% of AR14 from wastewater. In another study, Yadav et al. (2020), investigated the removal of Reactive Red 198 (RR198) from textile wastewater using chemical coagulation with ferric chloride and an upstream anaerobic sludge blanket reactor. The result of its integrated treatment showed that it was effective in removing 94.2% of RR198 from wastewater.

The results of these studies show that the combined chemical coagulation-biological treatment is an effective method for removing azo dyes from wastewater. However, the performance of the combined process can be affected by various factors such as the type and concentration of coagulants, pH, temperature, and the type of microorganisms used in the biological treatment. Therefore, further studies are needed to optimize the performance of the combined process and explore its applicability for different azo dyes and wastewater matrices.

3.3. Combination of Advanced Oxidation-Biological Processes for Removal of Azo Dyes

In recent years, combined Advanced Oxidation-Biological Processes have become an essential process for the pretreatment of azo-dye-containing wastewater. AOP technology can directly or indirectly cleave the conjugated double-bonded chromophore groups responsible for color, thereby improving the biodegradability of azo-dye-containing wastewater. Since ozonation can decompose azo dye molecules into smaller molecules, it is readily biodegradable in the activated sludge process (ASP). Biological treatment is another approach for the removal of azo dyes from wastewater. Microorganisms such as bacteria and fungi can break down azo dyes by enzymatic degradation. The degradation products are less toxic than the original dye molecule and can be further metabolized by other microorganisms. These processes can be used alone or in combination with each other, and they are very effective in removing azo dyes from wastewater(Ledakowicz and Paździor, 2021).

In a study conducted by Wu and Wang (2001) regarding the purification of wastewater containing azo dyestuffs by ozonation, it was noted that the transfer rate of ozone increased in relation to the initial dye concentration, applied ozone dosing, and temperature. The study concluded that ozonation could reduce chemical oxygen demand by 27% to 87% and increase the biodegradability of wastewater by 11 to 66 times.

Gökçen and Özbelge (2006) investigated pre-ozone treatment of aqueous acid red-151 (AR151) solution followed by purification using an activated sludge process. The study showed that pre-ozone treatment could enhance the biodegradability of azo dyes and improve the purification efficiency of the biological treatment process.

Lu et al. (2009a; 2009b) conducted a study on the treatment of azo dye-reactive bright red X-3B-containing wastewater using a sequential ozonation and upstream biological aeration filtration process. The results showed that the integrated process is a promising technique for the treatment of wastewater containing azo dyes.

The process of heterogeneous photocatalysis involving AOP converts stable organic compounds with high molecular weight into structures that are more biodegradable and smaller. However, this process takes a long time to degrade. Currently, the combination of photocatalysis and biological treatment has been extensively used to treat wastes that contain azo dyes. (Brosillon et al., 2008; Harrelkas et al., 2008; Mozia et al., 2009; Sudarjanto et al., 2006). The effect of fenton-treated acid dyes and reactive dye on aerobic, anoxic, and anaerobic processes was studied by Arslan-Alaton et al. (2008). They have been proposed the use of the Fenton process for complete color and partial organic carbon removal prior to biological treatment, without any negative effects on aerobic, anoxic, and anaerobic processes. Lucas et al. (2007) developed a sequential process involving Fenton's oxidation and aerobic biological treatment for decolorizing aqueous azo dye RB5, achieving a decolorization efficiency of approximately 91% at an initial concentration of 500 mg/L. The combination of Fenton's oxidation and aerobic SBR has been reported to be an effective method for significant biodegradation of azo dyes (Tantak & Chaudhari, 2006). García-Montaño and colleagues (2006) utilized an integrated photo-Fenton reaction with an aerobic SBR to biodegrade a commercial homo-bireactive dye (Procion Red H-E7B, 250 mg/L). The best removal efficiency was achieved with a photo-Fenton pretreatment of 10 mg/L Fe (II) and 125 mg/L H_2O_2 for 60 minutes in SBR and one day hydraulic retention time. However, the use of Fenton reagent can result in the aromatization of the dyestuff, and this process has several drawbacks such as the formation of aromatic amines, high reagent cost, and production of sludge containing high amounts of Fe (III). Therefore, further research is necessary to fully mineralize textile azo dyes and identify a cost-effective alternative treatment method.

In recent years, electrochemical methods applied to remove persistent organic compounds from textile wastewater have attracted great interest. Carvalho et al. (2007), investigated the electrochemical oxidation of Acid Orange 7 metabolites after anaerobic biotreatment using an upstream anaerobic sludge blanket reactor. It has been reported that persistent pollutants are almost completely eliminated and provide a COD removal of more than 70%.

Mahdizadeh et al. (2021), a hybrid UV/O_3/SBR (ultraviolet irradiation, ozone and sequential biological reactor) process was used for the removal of an azo textile dye (C.I. Reactive Red 195). First, azo dye was pre-treated with the UV/O_3 process. Then wastewater treatment was carried out using the SBR process. As a result of the study, the hybrid UV/O_3/SBR treatment is very effective in the removal of azo dye, the degradation and mineralization mechanisms of the process occur through hydroxyl radicals (OH•), ozone, bacterial activities and photolysis, and the azo dye removal is up to 98.3% has been reported.

The degradation of the azo dyestuff called orange II was investigated by Kim et al. (2005) using the electroenzymatic method with an immobilized horseradish peroxidase enzyme in a two-chamber packed-bed flow reactor. The researchers noted that the higher degradation rate achieved with this method was attributed in part to the adsorption of the orange II dye to the graphite felt, rather than using electrolysis alone.

Paździor et al. (2019), investigated the combination of existing and emerging AOP and biological processes in the treatment of industrial textile wastewater. Various AOP technologies (UV/H_2O_2, Fenton, ozone, etc.) and biological processes (activated sludge, membrane bioreactor, etc.) are discussed. The advantages and disadvantages of these technologies in treating industrial textile wastewater are discussed and evaluated. Furthermore, the potential and importance of combining AOP and biological processes in the treatment of industrial textile wastewater were highlighted, where combining AOP and biological processes can increase treatment efficiency and reduce energy consumption.

Qian et al. (2021), further treatment of dyestuff wastewater was investigated using an innovative Fenton-like /MnO_2 filled upflow biological filter bed system and a system equipped with modified ceramic granules. It has been stated that using modified ceramic granules together with Fenton-like technology and MnO_2-filled biological filter bed system increases the treatment efficiency of dyestuff wastewater and provides high efficiency in removing organic pollutants. In addition, it has been stated that these systems are advantageous in terms of environmental sustainability with low operating costs and energy consumption, as well as removing organic substances from dyestuff wastewater with high efficiency. It was emphasized that using Fenton-like/MnO_2-filled biological filter bed systems and modified ceramic granules could be an efficient and economical option for the further treatment of dyestuff wastewater. Studies on Integrated Advanced Oxidation-Biological Processes are of great importance for removing azo dyes. These studies investigate the effect of combining different advanced oxidation technologies and biological processes on removing azo dyes. This method offers a promising solution for effectively and sustainably removing azo dyes in industrial wastewater. Therefore, it is important in terms of wastewater management and environmental protection.

4. Treatment Processes Integrating Anaerobic and Aerobic Methods

4.1. Mechanism of Decolorization

Azo dyes acquire their color due to the presence of azo bonds, auxochromes, and conjugated double bond systems. Although the azo bond is resistant to aerobic degradation, it can undergo decomposition in anaerobic or anoxic environments, leading to color removal and the generation of aromatic amines. However, anaerobic color removal necessitates an additional carbon source. Electrons are generated as the extra carbon is converted into methane and carbon dioxide gas. Reactive dyes act as the terminal electron acceptor for these released electrons, leading to the reduction of the azo bond. Since this process does not occur in the presence of oxygen, the azo bond must first be broken under anaerobic conditions prior to the aerobic process (Mıdık, 2011). Chinwetkitvanich et al. (2000) found that the decolorization capacity of the process was increased with the optimum amount of tapioca starch used as an additional carbon source. Although azo dyes are relatively easy to reduce anaerobically, their products have been reported to be biorecalcitrant under anaerobic conditions (Xu et al., 2007). Bacterial azo dye biodegradation occurs in two steps, where the first stage involves the reductive cleavage of the azo linkages of the dyes. This often leads to the formation of colorless but potentially toxic and carcinogenic aromatic amines, which is one of the disadvantages of anaerobic treatment (Şahin, 2006). While dyes are usually not cytotoxic, mutagenic or carcinogenic, the amines formed due to anaerobic degradation can exhibit these properties.

As a result, it is recommended to use anaerobic systems as a preliminary treatment method before aerobic treatment. This is because aromatic amines can be effectively broken down in aerobic conditions by opening the ring of the aromatic compound and hydroxylation. By using an integrated anaerobic-aerobic treatment process, effective color removal can be achieved in the first step, followed by the removal of resistant aromatic amines in the aerobic step (O'neill et al., 2000b). The degradation of aromatic amines constitutes the second step, and this process is mainly aerobic in nature, as shown in Figure

6. With azo dyes being decolorized under anaerobic or anoxic conditions, and many aromatic amines being completely degraded under aerobic conditions, the anaerobic-aerobic sequential process can provide an effective solution for the complete treatment of wastewater containing azo dyes.

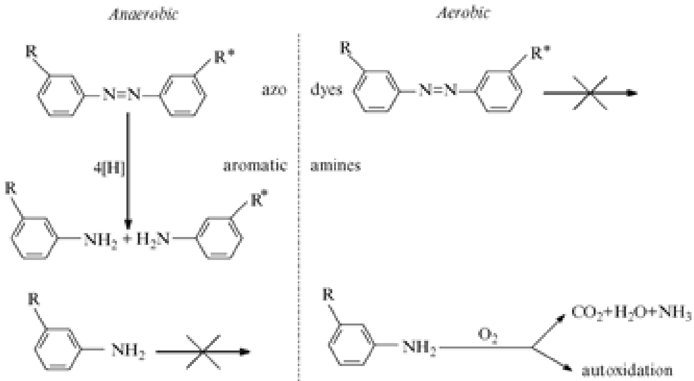

Figure 6. Recommended method for biodegradation of azo dyes in bioreactors (Lu & Liu, 2010)

4.2. Treatment of Azo Dye-Containing Wastewater through Combined Anaerobic-Aerobic Bioreactor Processes

Integrated anaerobic-aerobic treatment technologies are widely used in bioreactors for the treatment of wastewater containing azo dyes. These technologies allow the combination of anaerobic and aerobic conditions for the complete biological mineralization of azo dyes. This condition can be applied in a single reactor in the spatial separation of two sludges with a sequential anaerobic-aerobic or integrated anaerobic-aerobic reactor system (Azimi et al., 2021).

Integrated anaerobic-aerobic treatment systems can be carried out in separate reactors or a single reactor with appropriate timing of the anaerobic and aerobic phases. These systems can be temporal separation-based systems such as SBR or other alternative systems such as hybrid or micro-aerobic systems with ventilated zones (Ren et al., 2011). Azimi et al. (2021), investigated the treatment of textile dyeing wastewater containing three different reactive azo dyes using anaerobic-aerobic processes. It has been reported that the 3-stage anaerobic-aerobic process, in which the effect of a different number of stages and different bioreactor types on the removal of azo dyes, is more effective for the removal of azo dyes, and the immobilized cell reactors show higher performance than conventional suspended culture reactors. As a result, it is seen that anaerobic-aerobic processes are an effective option for the removal of azo dyes in industrial wastewater. Ravadelli et al. (2021), the treatment of azo dye-containing wastewater was investigated by integrating the electrocoagulation process into an anoxic/oxic membrane bioreactor for pretreatment. They reported that electrocoagulation using different electrode materials and current densities is an effective pretreatment method for removing azo dyes and provides higher efficiency when used with an anoxic/oxic membrane bioreactor. As a result, it is seen that the combination of electrocoagulation process and membrane bioreactor is an effective option for the removal of azo dyes in industrial wastewater. Kathawala et al. (2021), made a performance comparison between anaerobic and integrated anaerobic-aerobic biological reactor systems for the effective treatment of textile wastewater. It has been reported that both systems are effective for removing organic pollutants in textile wastewater and show similar performance in reducing organic load, but the integrated anaerobic-aerobic reactor system shows higher efficiency in terms of color removal and COD removal. As a result, it was emphasized that the integrated anaerobic-aerobic biological reactor system is a more suitable option for effectively treating textile wastewater. Khan et al. (2021), acid blue 29 azo dye was biologically purified using a system combining microbial fuel cell and aerobic bioreactor. It has been reported that a high rate of purification of acid blue 29 is achieved in the integrated system by using a system consisting of an air-cathode microbial fuel cell and an aerobic bioreactor, and it has been reported that the microorganisms used in the system contribute to the biodegradation of azo dyes. As a result, it is seen that a more efficient system can be created by combining different treatment technologies for the biological treatment of azo dyes.

The integrated anaerobic-aerobic treatment method is an effective method for the treatment of wastewater containing azo dyes. This method is accomplished by the decomposition of organic matter and separation of azo dyes in anaerobic bioreactors, followed by complete decomposition of organic matter and further separation of azo dyes by supplying oxygen to wastewater in aerobic bioreactors. However, the efficiency of this method depends on the characteristics of the wastewater and environmental conditions. Therefore, it is essential to design and operate suitable bioreactors for integrated anaerobic-aerobic treatment of wastewater. At the same time, in order to minimize the harmful effects of azo dyes on the environment, industrial enterprises should be careful about the production and use of azo dyes(Gadow and Li, 2020).

4.3. Impact of Bioreactors on Azo Dye Biodegradation

The effect of bioreactors on the biodegradation of azo dyes depends on the conditions under which the biodegradation takes place and on the design of the reactor. Two separate stages are required for the biodegradation of azo dyes: anaerobic and aerobic stages. The anaerobic stage is characterized by the activity of certain microorganisms that convert azo dyes into their reducing equivalents, aromatic amines. In the aerobic stage, aromatic amines and other intermediates are fully mineralized to carbon dioxide and water(Oliveira et al., 2020).

Bioreactor design has the capacity to control many factors that can affect the biodegradation of azo dyes. These factors include parameters such as pH, temperature, hydraulic retention time, Dissolved Oxygen, nitrate concentration, settled solid concentration, and mixing speed. The bioreactor design also provides suitable conditions to perform the anaerobic and aerobic steps required for the biodegradation of azo dyes. Another important factor that can affect the biodegradation of azo dyes is the chemical properties of the dye. Properties such as class and type of dye, dye concentration, side groups, and organic dye additives can affect the biodegradability of azo dyes. Some studies have shown that reactive azo dyes biodegrade more easily. Also, low dye concentrations may increase the biodegradation of azo dyes, while higher concentrations may have an inhibitory effect. In conclusion, bioreactors play an essential role in performing the anaerobic and aerobic steps required for the biodegradation of azo dyes. Bioreactor design and chemical properties of the dye are among the factors that affect the biodegradability of azo dyes (Shi et al., 2021).

The structure of azo dyes significantly affects the rate of azo dye biodegradation. Some dyes biodegrade faster than others, depending on the number and location of azo bonds. Brown and Laboureur's research show poly azo dyes are less likely to degrade than mono or diazo dye type (Brown & Laboureur, 1983). Suzuki et al. found a link between the aerobic biodegradability of 25 sulfonated azo dyes and their chemical structures (Suzuki et al., 2001). In another study, algae biodegradation of azo dyes by algae was investigated. This process was found to be related to the molecular structure of the azo dye and the algae species used (Jingi & Houtian, 1992). The more azo bonds are broken, the slower the reduction rate will be. A few studies showing a positive correlation with decolorization efficiency have been associated with the hydraulic retention time of the anaerobic stage (Rai et al., 2007). However, the initial dye concentration of wastewater containing azo dyes is also an essential factor to be considered. Seshadri et al. (1994), concluded that dye concentration could cause a decrease in the percentage of dye removal. Also, inhibition may occur in direct relation to the effects of increased dye metabolite formation due to higher dye concentrations. Carliell et al. (1995), stated that C.I. Reactive Red 141 was inhibitory against anaerobic organisms at concentrations greater than 100 mg/L. The pH value of wastewater can affect the correct function of both anaerobic and aerobic organisms (Grady et al., 1999). Wuhrmann et al. (1980), studied the effect of the pH value of the wastewater on the dye removal rate. They observed a significant increase in the decolorization rate with decreasing pH values. Also, wastewater from the textile and dyestuff manufacturing industries contains a significant amount of salt in addition to azo dye residues. Khalid et al. (2008), on the other hand, found an inverse relationship between the rate of decolorization and the salt concentration. For this reason, biological treatment systems are often recommended to dilute high salt concentrations or pre-treat wastewater containing azo dyes using salt-tolerant bacteria. The reduction rate of azo dyes is affected by nitrate and oxygen levels. Wuhrmann et al. (1980), showed that azo dyes could decolorize under forced aerobic conditions. However, high nitrite concentrations in activated sludge plants can significantly inhibit dye removal.

Bioreactors play an essential role in the biological treatment of azo dyes. Bioreactors allow microorganisms to grow under suitable conditions, perform their metabolism and biodegrade azo dyes. In this process, many factors affect bioreactor performance (Figure 7) (Pande et al., 2019).

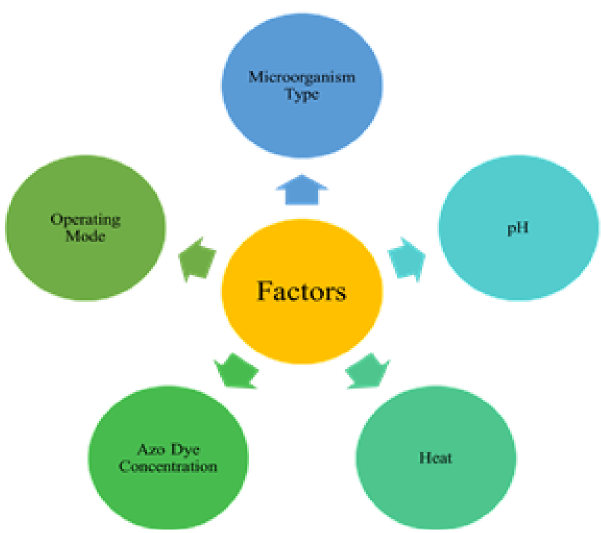

Figure 7. Factors affecting decolorization of azo dyes (Pande et al., 2019)

The studies mentioned above show that the factors in the effect of bioreactors on azo dye removal are:

1. Microorganism type: The microorganism type used in the bioreactor is the most crucial factor affecting the biodegradation of azo dyes. Different species may have different effects on different azo dyes.

2. pH: The pH value of the bioreactor significantly affects the activities of microorganisms. The optimum pH range allows microorganisms to perform at their best.

3. Temperature: The bioreactor's temperature significantly influences microorganisms' activities and the biodegradation of azo dyes. The optimum temperature range increases azo dye removal by increasing the activity of microorganisms.

4. Azo dye concentration: Bioreactor performance may vary depending on the azo dye concentration. Higher concentrations may reduce azo dye removal by reducing the activity of microorganisms.

5. Operating mode: The bioreactor's operating mode significantly affects the biodegradation of azo dyes. Continuous operating mode provides better removal of azo dyes.

The results show that they are cutting-edge technologies in integrated processes for treating wastewater containing azo dyes, based on many recently published references. This article demonstrates that combined processes will replace traditional technologies used for color removal and are promising alternatives. These processes have the advantages of being highly effective in azo dye removal, inexpensive, non-toxic end products, and biocompatibility.

5. Conclusion

The treatment of wastewater containing azo dyes with integrated processes is an essential step in preventing environmental pollution. This type of wastewater may occur due to many reasons arising from industrial activities. The azo dyes in these wastewaters are generally harmful and toxic to the environment.

There are several techniques employed in the management of azo dyes, including advanced oxidation processes, biological treatment, chemical oxidation, adsorption, and membrane filtration. However, each method has its advantages and disadvantages. For example, the chemical oxidation method uses oxidation reagents to reduce the solubility of azo dyes. This method can effectively reduce the organic components of wastewater but may pose a risk to the environment due to the formation of toxic by-products. Biological treatment is based on the treatment of wastewater through natural biological activities. This method can lead to the biodegradation of the organic components of the wastewater and the formation of relatively less toxic by-products. Membrane filtration is accomplished by filtration of wastewater through a membrane. This method can reduce the solubility of azo dyes and does not cause changes in the chemical composition of the wastewater. However, membrane filters can be costly as they require frequent cleaning and maintenance. The adsorption method is based on the adsorption of azo dyes through adsorption materials. This method does not result in the effective removal of azo dyes and the formation of toxic by-products. Advanced oxidation processes involve the use of different chemical reagents for the degradation of azo dyes. This method allows azo dyes to break down effectively and minimize the formation of toxic by-products.

Integrated processes involve many methods and can help purify azo dyes more effectively. However, the implementation of these processes requires a treatment strategy designed to achieve cost-effective and efficient results. Treatment using integrated advanced oxidation-biological processes is often recommended. Among these techniques, photocatalysis and sequential biological treatment are the most common. To decrease azo compounds into aromatic amines, anaerobic conditions are necessary, and bacterial biodegradation of aromatic amines primarily occurs under aerobic conditions. Hence, the most efficient way to eliminate azo dyes from wastewater is through an integrated anaerobic-aerobic bacterial process.

As a result, the treatment of wastewater containing azo dyes with integrated processes is essential for reducing the environmental pollution. Different treatment methods can help to effectively remove azo dyes and minimize the formation of toxic by-products. However, each treatment method has advantages and disadvantages, and the appropriate treatment strategy should be determined according to the characteristics of the wastewater and environmental conditions. However, wastewater treatment can be costly, and it is important to consider costs and effectiveness to create an economically sustainable treatment strategy. In the future, developing more sustainable and efficient treatment methods can reduce the difficulties and costs of wastewater treatment. In addition, wastewater reuse is important in protecting water resources and supporting sustainable development. Future research needs to focus on issues such as the reaction mechanism of azo dye removal, the use of real wastewater, and large-scale experiments. Exploring mechanical and mathematical models to optimize the integrated process and characterize the interaction between reactants and azo dyes is also essential.

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CHAPTER VI

NANOTECHNOLOGICAL DEVICE MANUFACTURING AND OBTAINING COMPOSITE MATERIAL FOR DRY AGRICULTURE

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1. Introduction

Natural fibers are an important source for the production of polymers that are highly applicable in their nanoforms and can be used in a wide range of fields such as water/wastewater treatment, biomedicine, food packaging, harvesting and energy storage due to their high specificity. These natural nanofibers can be produced mainly from plants, animals and minerals, as well as from agricultural wastes. They can supplement these natural fibers with some substances, such as nanomaterials, to strengthen them. Natural or biofibre-reinforced biocomposites and nanobiocomposites are considered better than conventional composites. Sustainable application of nanofibers in agricultural sectors is a promising approach and could include plant protection and growth through encapsulation of many bioactive molecules or agrochemicals (i.e. pesticides, phytohormones and fertilizers) for intelligent distribution to targeted areas (Bulus et al., 2019).

The food industry and processing are very important application areas of nanofibers, especially active-intelligent food packaging and food packaging, which can include the use of nanofibers for food freshness indicators. Removal of pollutants from soil, water and air is an urgent area for nanofibers due to their high efficiency. Many new approaches, such as the use of nanofibers as indicators of CO and NH_3, or applicable agricultural areas for nanofibers are expected in the future.

Aeroponic farming is a farming method in which the roots of plants are constantly in contact with the air and the nutrient solution is sprayed onto the roots. In this method, plants provide nutrients and oxygen directly to their roots without the need for soil or growth medium.

The basic steps of aeroponic farming are:

1. Root System Formation:

In aeroponic farming, the roots of plants are released and kept in contact with the air in a suspended medium or in a special container. It is recommended to use a special pot to ensure the contact of the roots with air. The roots are exposed to the nutrient solution sprayed from the spray nozzles.

2. Preparation of Nutrient Solution

You need to prepare a nutrient solution specific to the aeroponic system. The basic nutrients needed by plants should include nitrogen, phosphorus, potassium, calcium, magnesium and trace elements (iron, zinc, copper, etc.).

Commercial aeroponic nutrient solutions usually contain a balance of these nutrients.

3. Installing the Spray System

In the aeroponic system, the roots of the plants are sprayed with a nutrient solution. For this, a system consisting of a pump and spray nozzles is used. The pump sprays the nutrient solution through the nozzles into the roots. It is important that the spray system works properly and that it is distributed homogeneously to the roots.

4. Providing Light

Plants need the right amount of light to grow. Since aeroponic systems are often used indoors, it is common to use artificial light sources. You may need to make lighting arrangements to provide the proper light spectrum (usually LED lights) your plants need.

5. pH and EC Control

In the aeroponics system, it is important to regularly check the pH and electrical conductivity (EC) levels of the nutrient solution. Different plants grow better at different pH ranges. Therefore, the pH level of the nutrient solution should be adjusted to suit the plant's needs. For healthy growth of plants, proper pH (usually between 5.5-6.5) and EC values (depending on the plant) must be maintained. The electrical conductivity (EC) of the nutrient solution determines the concentration and density of the nutrients it contains. Appropriate EC levels must be maintained for the healthy growth of plants. High EC levels can harm plants, while low EC levels can cause inadequate nutrient uptake. Appropriate EC values should be determined and regularly monitored, depending on the plant species and developmental stage.

To set up an aeroponic system, you must first obtain the materials you need. These materials include an aeroponic tank, a pump, a nutrient solution preparation system, a pH meter, an EC meter, a timer and plant trays. You will also need the appropriate light source for the plants to grow.

Below are the general steps for aeroponic system setup:

1. Prepare the aeroponics tank: The aeroponics tank is a unit that houses the trays you will use to place the roots of the plants. Above the tank are LED lights that illuminate the tops of the plants inside the trays. As a first step, choose a suitable place to place the aeroponics tank.

2. Nutrient solution preparation: You need to prepare the right nutrient solution to meet the nutrient needs of the plants. Using the nutrient solution preparation system, mix the right amount of nutrients into the water and fill the solution into the tank. Remember to ensure the correct levels by using pH and EC meters during the nutrient solution preparation process.

System Advantages-Why Dry Agriculture?

• Temperature control can be provided.
• Prevents the use of too much water. It saves water consumption.
• It prevents insect infestation and fungus formation in the soil.
• Can be used indoors without garden or land. Ideal for an urbanized area.
• To get more efficiency

Space saving

• Roots can grow without mixing
• To prevent costs such as soil aeration and fertilization need.
• Prevents diseased plants from infecting healthy plants (positioning the roots in different pots)

Drip Irrigation System in Yurdis

Water is dripped onto the soil at a low rate through a system of small diameter plastic pipes surrounded by outlets called drippers. It does not wet the entire soil, as in rain or normal irrigation systems, and provides water transmission to the root and root environment in the drip irrigation system. Drip irrigation is more frequent compared to other methods and provides a higher level of moisture in the soil at which plants can thrive. This, in turn, delivers the required amount of water and nutrients directly to the plant root for the proper growth and development of plants. At the same time, the use of fertilizers can be optimized in this way' (Simanungkalit et al., 2023).

Hydroponic and aeroponic systems have been introduced and the humidity of the water will be used in our target study. Organic agriculture will be promoted by using nanofiber membranes and ensuring the germination of seeds from the moisture of the water. In our target study, solutions will be presented to two important issues. The first is plant breeding material production and the second is waterless agriculture.

Polymers are one of the main uses of daily life. It is ensured that polymers are combined with different production techniques and turned into value-added products. One of these production techniques is the multidisciplinary field of nanotechnology. Functional materials produced with nanotechnological production techniques; It is used for purpose in sectors such as health, defense, textile, food, filtration and agriculture. Electrospinning technique, which is a nanofiber membrane production technique by means of electrical field from polymer solutions, is a nanotechnological method and is the most widely used functional material production technique when literature studies are examined (Breseghello et al., 2013; Clifton-Brown et al., 2018; Smith et al., 2016). However, not all of the various polymers such as thermoset and thermoplastic can be produced in the fiber production electrospinning system. Today, there is no polymeric fiber and particle production device in which all polymers are used in one system. While some polymer groups can be dissolved with solvents, some polymer groups are in mass and are melted as a result of heating to produce fiber. These devices prevent the use of both high-cost and functional materials. Inability to control the desired nano-scale production in terms of technical features of electrospinning, aerospinning, meltspinning and electrohydrodynamic atomization (EHDA) systems, the inability to use all polymers and additives in all four systems, the high cost of each device, and the functional material Due to their limited production, new technologies were being sought. Due to the technical limitations of these four production methods, hybrid productions have recently started to be preferred. A membrane was produced with electrospinning technology, and a membrane was produced with melt spinning technology, and hybrid material was produced through various interbinders and process combining techniques. While the productions obtained with hybrid technologies could be weak in terms of various properties such as strength, they could result in high costs.

Plant breeding is accomplished by controlled self or cross pollination and usually involves isolating the flowering parts of the parent plants (Buluş et al., 2020).. In the market, mostly paper-based pollination control bags are used for plant breeding in this way. However, since these pouches restrict the light required for the biological process, they can limit the speed of the breeding process and increase the costs. Also, the paper-based ones you can use for rain, wind, etc. it becomes unusable by tearing under weather conditions (Breseghello et al., 2013). Therefore, there is a need for new generation materials that are more permeable and transparent, durable and cost-effective for plant breeding. In fruit and vegetable production, there are problems that waste and wastage are high as a result of excessive use of water, organic agriculture cannot be fully achieved, and a production that is free from insects and pests is in question. There may be problems in plant protection that may threaten the life of the plant. Their solutions can be costly. Again, the main reason for this study in the case of waterless agriculture is the excessive use of our water. As a result of misuse of juice in fruits and vegetables, large amounts of waste may be lost, resulting in both a decrease in productivity and healthy production problems in agricultural production. It is also taken into account that the pests will be transmitted more easily.

Two important studies will be continued in this study. It is the production of membranes that will provide protection in waterless agriculture and plant breeding. Sustainable nonwoven surface materials made of recycled polymers will be developed that will increase the yield in plant breeding, provide thermal regulation in the microclimate of the plant and protect the plant from external effects such as rain, wind and bird attacks. The basis of developing the product in this study is by adding heat-storage/thermal-regulating material obtained from recycled materials to non-woven surfaces made from low-weight and recycled polyester and/or polypropylene (PP) raw materials, both by enabling the plant to make thermal regulation in its microclimate and also to protect the plant in many ways. It is based on increasing plant breeding efficiency by protecting harmful external factors (Michael et al., 2020). At the present stage, nonwoven surface materials can be produced at affordable costs by many companies that have a voice in this field in our country. Considering the production of textile fabrics, there is a very economical production process since there is no yarn stage in the production of nonwoven textile surface (Buluş et al., 2021).

The production of materials that provide thermal regulation function to nonwoven surfaces can be done in the current laboratory environment in our country, as mentioned before, through the synthesis/production of solid-solid phase-changing materials. Polyethylene glycol (PEG) etc. as material. solid-solid phase change materials will be doped to the nonwovens in a cross-linked form. In the second stage, industrial partnership is needed in order to reach the final prototype by industrial production. Membrane will be obtained with the air spray system, which is a nanotechnological method that can eliminate the waste of water and fruit and vegetables. Controlled organic agriculture will be realized with a healthy production. Our research team is working on seed tape against bacteria and viruses. Based on this study, the membrane design to be used in waterless agriculture and plant breeding is based on. In the membrane producing system, our team produces DOMESTIC. With our device, the membrane will be produced and the produced membrane will be insect and bacteria-proof, provide humidity, breathe, and will fulfill the necessary conditions from seed to sprouting.

Since there is no study in our country that includes the use of nonwovens in plant breeding, it is a first for our country. In addition, it is a first in the world with its use of thermal regulation function especially in plant breeding. At the end of the study, the nonwoven material, which will be produced on an industrial scale, will increase the efficiency in plant breeding, as well as protect seeds, prevent fungus formation and protect plants from external factors such as rain, wind and bird attacks. In the next stages of the study, it is aimed to focus on patent, brand and commercialization studies and to present a globally competitive product in the field of travel hygiene. Each mentioned step includes innovation steps and new claims that will be the subject of patents and utility models. It is among the unique methods in the world in terms of the fact that suspended agriculture will be carried out by making use of the moisture of the water in our product.

The main output of the study is the treatment of the theme of make our water valuable and shape your future. The study has no analogues in Turkey, it is the first in its field in Turkey. The transition to non-woven surface-based plant breeding materials instead of paper-based pollination pouches has been made in the last few years in countries such as the Netherlands, Japan and the USA, where pioneering studies have been carried out in agriculture, but as in this study, smart non-woven surfaces with heat storage and thermal regulation ability have not yet been scientifically implemented. It is not in commercial use either. It has a high level of applicability due to the easy supply of phase-change materials to be used in the study, the easy availability of nonwovens locally, and the technical textile development experience of the working team based on many years.

The nonwoven surface product developed in the study was first used in the field of agricultural technical textiles (Agrotech), corn etc. It will be used in the cultivation and product quality improvement and breeding applications of the products. Since we will continue to work with phase-changing materials, it will not pose a problem at the point of application. By preventing the waste of water, fruit and vegetables, healthy product production will be ensured with organic agriculture. The market share of our country will continue to increase in the world. This study will create added value in the agriculture sector by providing the waterless agriculture practice and the values that must be taken from the soil through the membrane, ensuring the passage of the water to the seed by taking advantage of the moisture, preventing the passage of bacteria and insects, as well as providing an adequate oxygen environment. It is important to produce nanofibers from different agricultural wastes and to apply nanofibers for food packaging.

As the research team, we know that our water is important for our Earth, and promoting the protection of our water is among the aims that we have conveyed and want to convey within the scope of the study.

Within the scope of the study, membranes for device production and waterless agriculture were obtained together with the device.

2. Material and Method

Energy applications have become a subject of great interest in wearable electronics and smart clothing in textiles. It is a sought-after function for a garment to cool the wearer in a hot environment and, on the contrary, to warm it up when entering a cold environment. It has not yet been applied in agricultural textiles.

In this study, fiber spinning method was applied. FDMs will be applied both in microcapsule form and directly on textile surfaces with the help of laboratory-type padding. In our study, polyethylene glycol (PEG) was used as phase change material. By using biodegradable polymer, the necessary environment for waterless agriculture will be provided by using an air spray system. The efficiency of the seed from the soil will be gained to the nanofiber membrane. In this way, the membrane will prevent the passage of bacteria and insects, and what needs to be taken from the soil for the seed will be taken. Various waste materials, biopolymers and seeds were used for this.

The target audience of the study is agricultural product breeders, individuals and/or companies that carry out plant breeding and companies that sell agricultural textiles. Dry farming, paper-based pollination bags etc. images of pollination sacs based on non-woven surface are shown in Figure 2.1.

Figure 2.1: Dry farming, paper-based pollination bags etc. images of nonwoven surface based pollination pouches

Our waterless farming system and airbrush spraying system are shown in Figure 2.2.

Figure 2.2: Our waterless farming system and our airbrush spray system

In our target study, plant breeding material and nanotechnological membrane production that will provide waterless agriculture and seed growing in waterless agriculture system have been provided. Within the scope of the study, device production was provided and membrane productions were carried out with the device.

3. Results and Discussion

In the first stage, nanotechnological membranes containing PEG material with FDM feature as plant breeding material will be added to the polylactic acid (PLA) polymer solution and sprayed with an airbrush to ensure that the plants are placed on their heads. In this way, bird attacks and losses will be prevented. PLA polymer was dissolved in dimethylformamide (DMF)/acetone (AC) solvent.

In the second stage, nanotechnological membranes for our ANHYDROUS AGRICULTURE system were obtained by airbrush airspray system by supplementing the polyvinyl alcohol (PVA) polymer solution with nutrients that contribute to the germination of the seed containing the nutrients in the soil. The obtained membranes were integrated into the waterless farming system. The PVA polymer will dissolve in the pure water. In the waterless farming system, there is pure water in a container. There is a heater under the pure water system, and the moisture in the air coming with the heat is sprayed with the air flow. The sprayed moisture was contacted with the nanotechnological membrane in the porous lattice. Thus, the membrane was slowly dissolved and food and moisture were brought into contact. The germination of the seed will be ensured and field studies have been carried out. Our nanotechnological production device is in Figure 3.1 and the membrane and nanofiber image we produced for waterless agriculture and plant breeding is in Figure 3.2.

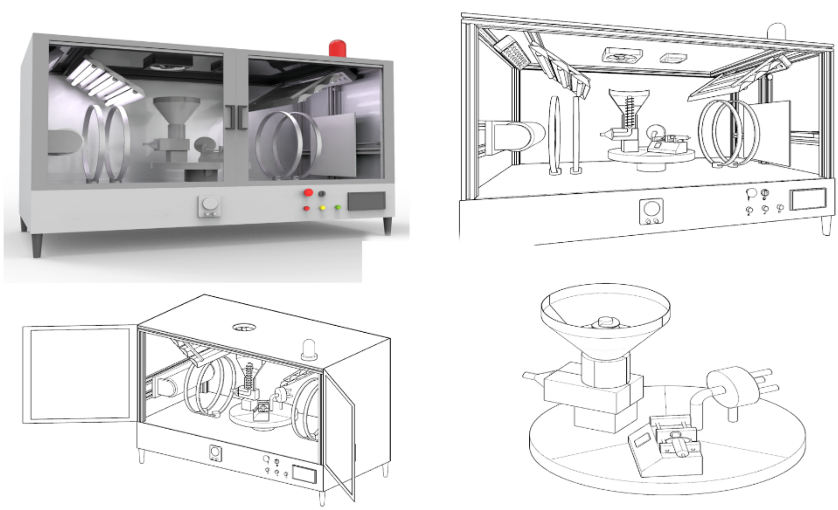

Figure 3.1: Our nanotechnological production device

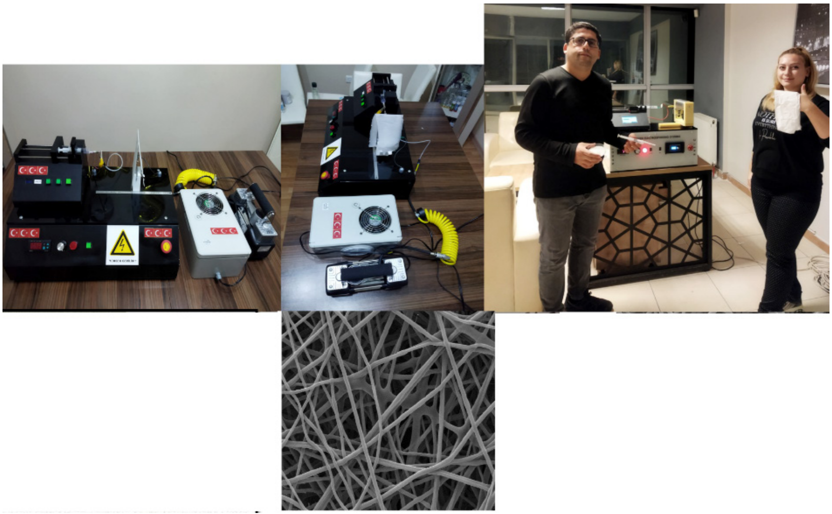

Figure 3.2: Membrane and nanofiber image for waterless agriculture and plant breeding that we produced

4. Conclusion

Within the scope of the study, four different production techniques were brought together in a single device to produce membranes for waterless agriculture. The use of water is valuable for the world for the future. With this awareness, the moisture formed by an air spray system by heating and humidifying the water will come into contact with the membrane we will produce. Nutrient values in the soil in the membrane will be released gradually. And since both the moisture and the nutritional values in the soil are contained in the membrane, the seed will contact the seed and it will gradually mature in the nanotechnological membrane cage that insects and pests cannot pass through. From this point of view, our membrane has a hydrophilic character and can dissolve in water. It can be ensured that the seed remains for a period of time until it sprouts. Our aim is to work for a healthy future, avoiding waterless (utilizing the moisture of the water) agriculture, organic (free from insects, pests and pesticides) agriculture, wrong irrigation and waste problems.

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CHAPTER VII

AFAD-FRIENDLY PORTABLE ELECTRO SPRAY BIOPRINT BLEEDING STOPS AND TISSUE REPAIR SYSTEM

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1. Introduction

The global nanofiber market size is estimated to be US$785 million in 2021 and is expected to reach US$3350 million by 2030, registering an 18% CAGR over the forecast period (2022– 2030). North America has the largest share, holding approximately 37% of the total nanofiber market. The market for polymeric nanoparticles is estimated to be worth $551.9 million in 2020 and will reach $1,511.8 million by 2030. The size of the global 3D bioprinting market was worth US$1.7 billion in 2021 and is expected to grow at a compound annual growth rate (CAGR) of 15.8% from 2022 to 2030 (https://www.coherentmarketinsights.com/market-insight/nanofiber-market-5129). The growth of this market is attributed to a limited number of organ donors and an increasingly aging population with chronic respiratory disease. Increasing R&D investment, technological advancement, and increasing incidence of chronic diseases are other vital influencing features that are likely to drive market growth over the forecast period. The 3D printing community is responding to the COVID-19 crisis by pledging to support the production of vital medical equipment for hospitals grappling with this pandemic. Our work, which offers solutions specific to products with a serious market size, has potential production opportunities that can close the gap in many areas in foreign markets of our country. It is a product with high export potential. It is a study that creates the potential to compete with foreign markets and domestically. Although import substitutes are single and hybrid models, we do not have a fully functional device, but based on our market preliminary research and negotiations, a system that can produce value-added products that will close the gaps in many sectors is offered. Sustainability will be ensured within the scope of device sales, innovative product R&D and technical support and product R&D. While our device has a portable electrospinning part, there are no two systems together with its portable bioprinter part. It is a system that should be in everyone's home as well as in all businesses, shopping malls, ambulances and health institutions. Wastes, polymers, herbal products, etc. In addition to the production of fibers and particles from a wide variety of substances that come to mind, it can be taken in pressures to fill deep wounds. While the electrospinning system is a nanofiber production system from polymer solutions with electrical field, the bioprinter is a 3-dimensional system that prints tissue material to be used in tissue engineering. However, both are heavy-duty systems. Although hybrid and single module pressures are added to the wound depth according to the depth of the wound formations, the lack of regular production and healthy application causes the benefit of not being able to fully close the wound area to become infected and the wound area to heal late. Within the scope of this study, a system that offers the possibility of spraying the wound area during the emergency response or curing with UV light during the pressure of the wound liquid and/or gel by combining it with the wound healing solution prepared by our research team beforehand using a converter, has been produced as an Disaster and Emergency (AFAD)-friendly pen.

The traditional method for wounds found in animals in Figure 1.1 is also difficult to lay and dress the animal. However, the device was developed within the scope of the study to enable outpatient treatment.

Figure 1.1: Deep and infected wounds

The electrospinning-bioprinter system developed in the study becomes qualified within the scope of R&D studies. A qualified R&D activity is carried out with a disciplinary approach, with the competence of the research team, with its rich infrastructure in terms of both nanoparticle, fiber, 3D tissue material and characterization. With the combination of electrospinning and bioprinting system, it provides solutions to deep wounds, stopping bleeding, allowing the wound to breathe, providing flow absorption, preventing bacteria from passing and creating a basis for tissue growth. In deep benefits, it prevents scar formation and provides skin tissue integrity. It is a system that offers purpose-oriented production to all sectors. For this reason, it is a study that offers functional use and should be in all R&D centers. With the device, it is also a system that offers the opportunity to produce many, many different products such as wound healing tape, dialysis membrane that filters the blood for the dialysis patient, nanoparticles that can release drugs, skin masks, filters that do not allow viruses and bacteria, and artificial vessels. In the portable dialysis machine of our team, a nanotechnological filter that can filter the blood that performs the dialysis process in the system and retain harmful toxins has been obtained within the scope of our device (Buluş et al., 2020; Liu et al., 2020; Yan et al., 2019). With our patent application system, significant contributions will be made to end foreign dependency.

2. Material and Method

Before the device production, the design was provided with a 3D design program. The 3D production of the design was produced in a 3D printer. The circuit and electronic card are provided by our team. The whole system was combined and made ready for production. Patented content with polymer matrix to be used will be obtained and production trials have been provided with the device.

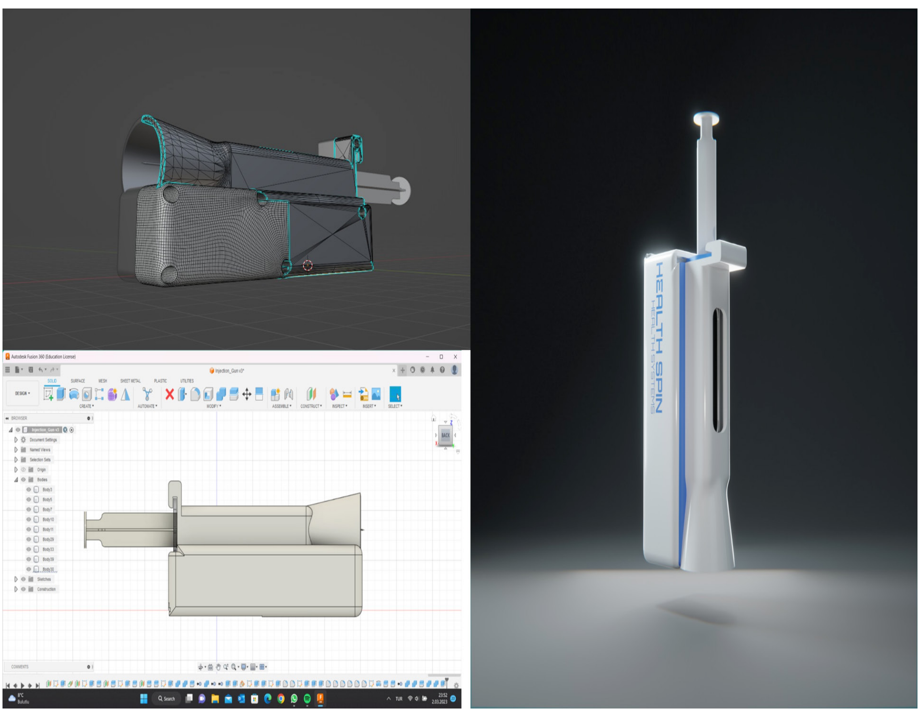

Figure 2.1: Our AFAD-friendly pencil 3D drawings

AFAD-friendly pen was produced, and production trials were provided by preparing a hydrophilic polymer solution such as polyvinyl alcohol (PVA).

3. Results and Discussion

When the results of the study were examined, an AFAD-friendly pen was produced and a nanofiber membrane was produced from water-soluble PVA polymer. When the FEGSEM morphological image was examined, it was determined that the fiber diameter was in the range of 200-450 nanometers (Buluş et al., 2021; Revia et al., 2019; Yan et al., 2019). AFAD friendly pencil Figure 3.1 and the membrane and nanofiber image produced with AFAD friendly pencil spindle are shown in Figure 3.2.

Figure 3.1: Our AFAD-friendly pen production

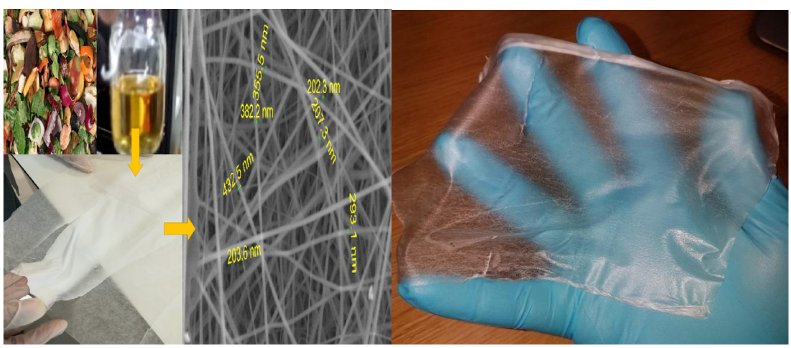

Figure 3.2: Membrane production and nanofiber images

4. Conclusion

Within the scope of our study, AFAD-friendly pen was produced successfully and production trials were taken. As our target audience, our

AFAD-friendly pen can be used in ambulances in the first place for emergencies, hospitals, shopping malls, houses, schools, etc. It will offer advantageous use that does not take up much space in communities where there is a communal life or in the bags of individuals for personal use. There is a 5% risk. In the case that the optimization is provided and the B plans are implemented, there will be no problem posing factor in the study.

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CHAPTER VIII

METAL HYDROXIDE ELECTRODES FOR SUPERCAPACITOR APPLICATIONS

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1. Introduction

Along with increasing energy consumption, energy supply also creates some challenges (Nguyen and Montemor, 2019). Energy demand is projected to more than double by 2050 and more than triple by the end of the 21st century (International Energy Agency (a) 2017; (b) 2012). Fossil fuels are the main energy generation sources and provided about 81.6% of global energy in 2015. However, greenhouse gas emissions, especially CO_2, cause serious global warming and environmental problems (Shafiee and Topal, 2009). Renewable energy sources are critical because of the adverse environmental conditions resulting from dependency on fossil fuels (Tezel et al., 2021). As a result, sustainable and renewable energy sources, under economic and social roadmaps and strategic plan, are accepted as the main theme for the United Nations Sustainable Department in 2030 (Lewis et al., 2005; Cf, O. D. D. S., 2015).

However, it also brings problems the dependence on the time of day and weather conditions of renewable energy sources (Shaikh et al., 2022). Regardless of whether the energy is time-independent and the availability of energy sources, energy storage technology needs to be developed in order to produce energy (Allaoua et al., 2017; Lin et al., 2016). Also, electronic circuit elements produced using semiconductors have become a basic need in every aspect of human life (Meydaneri Tezel and Tezel, 2023-a). To overcome these problems, two types of electrochemical energy storage systems (EEDSs), batteries, fuel cells and supercapacitors should be developed further (Shaikh et al., 2018; Shaikh et al., 2021-a; Shaikh et al., 2021-b, Tezel and Tezel, 2023-b). The batteries feature stable linear discharge at high specific voltage and high energy density for commercial applications (Ye and Feng, 2014). However, their use is limited due to their low power density, low cycle life and explosive properties (Nitta et al., 2015). Supercapacitors, known as Faraday quasi capacitors or electrochemical capacitors (Guan et al., 2020), are developing energy storage devices and with high specific capacitance in energy storage technology. In particular, electrochemical capacitors (ECCs) are important candidates due to their high power density, long cycle life (>100,000 cycles), fast charging and discharging, favorable temperature, use of low cost materials (Vidhya et al., 2020), and rapid burst power supply applications, especially electronically and electrically (Tezel and Tezel, 2023-b; Tezel and Tezel, 2023-c; Gogotsi & Huang, 2021).

The output power of the supercapacitor is higher than that of the battery, but lower than that of a capacitor. However, the specific energy is highest for supercapacitors. Supercapacitors also have the advantage of high power performance under 40 °C, which is a difficult situation for batteries (González et al., 2016). Another advantage of supercapacitors is their safe nature, reaching high power during charge-discharge (Panda et al, 2020; Balakrishnan & Subramanian, 2014). The main advantage of supercapacitors is their high stability due to their charge storage mechanism. Charge-discharge processes do not include electrode volume change due to reversible processes. In contrast to the battery charge storage mechanism, an irreversible redox reaction occurs in the bulk of the material. However, the biggest disadvantage of supercapacitors is the low operating potential window (Panda et al, 2020). Too high applied potential results in decomposition of the electrolyte. Energy storage systems (ESSs), such as batteries and supercapacitors, play a middle key role in amplifying power transmission and with the fundamental nature of renewable energy sources (wind and solar power) (González et al., 2016).

Supercapacitors do not only discharge in a matter of seconds where bursts of power are required, but also charge in a matter of seconds, but their high energy storage densities are essential as dynamic braking of transmission systems

(Shaikh et al., 2011-a; Shaikh et al., 2011-b; Nitta et al., 2015). Applications of supercapacitors in the automotive industry are to boost the efficiency of hybrid electric vehicles (HERs). In addition, fuel cell/supercapacitor combined technologies bring improvements to the charge/discharge cycle performance of HERs.

Various types of efficient supercapacitors are produced to meet all kinds of the increasing demand in modern applications such as including powering the electronic equipment of trains, portable electronic devices, energy backup systems, automobiles, aircraft, security alarm systems, power supply systems (UPS), light emitting diodes (LED) and flashlights (Narayanan & Joseph, 2018, Shaikh et al., 2011). The key element that determines the performance of the supercapacitor is the electrode. Metal hydroxides as electrode materials show better energy density due to their higher specific capacitance than typical carbon-based double-layer supercapacitors and electronically conductive polymers. They are also more chemically stable, easily prepared, more compatible with electrolytes, environmentally friendly, more durable and cost-effective (Narayanan & Joseph, 2018). This section discusses high performance potential metal hydroxide electrodes for supercapacitors.

2. Types of Supercapacitors

According to the studies, supercapacitors are divided into three categories: electrochemical double-layer capacitors (EDCL), pseudocapacitors and hybrid capacitors (Figure 2.1). Each class has its own charge storage mechanism. These are, respectively, non-faradic, faradic, and a combination of the two.

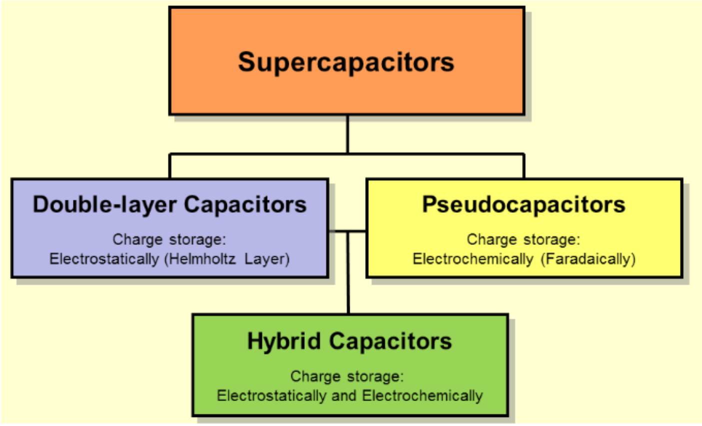

Figure 2.1. Types of Supercapacitors (Bueno, 2019).

2.1. Electrochemical Double Layer Capacitors (EDCL)

Electrochemical double-layer capacitors (EDLC) are formed from two carbon-based electrodes, an electrolyte and a separator (Figure 2.2). In EDLC, it is similar to conventional two-plate capacitors with its energy storage and transmission mechanism. Physical charge storage occurs at the interface of the electrode and electrolyte. During the charging process, electrons are transported externally from the negative electrode to the positive electrode. During the discharge process, electrons and ions are transported in reverse (Tang et al., 2011). When voltage is applied, charge builds up on the electrode surfaces. Following the natural attraction of different charges, ions in the electrolyte solution diffuse across the separator into the pores of the opposite charge electrode. However, the electrodes are designed to prevent recombination of ions. Thus, a bilayer charge is formed at each electrode. These two layers, combined with an increase in surface area and a decrease in the distance between electrodes, allow EDLCs to achieve higher energy density than conventional capacitors (Burke, 2000; Conway, 2013). Therefore, the energy storage mechanism is non-Faradic without a redox reaction. That is, there are no chemical changes associated with non-faradic processes, as there is no charge transfer between the electrolyte and the electrode. Thus, only physical charge transmission occurs between electrode and electrolyte, virtually no change in volume or morphology of the electrode material, resulting in a long cycle life of EDLC (Narayanan & Joseph, 2018). Therefore, charge storages in EDLCs are reversible, allowing very high cyclic stability to be achieved.

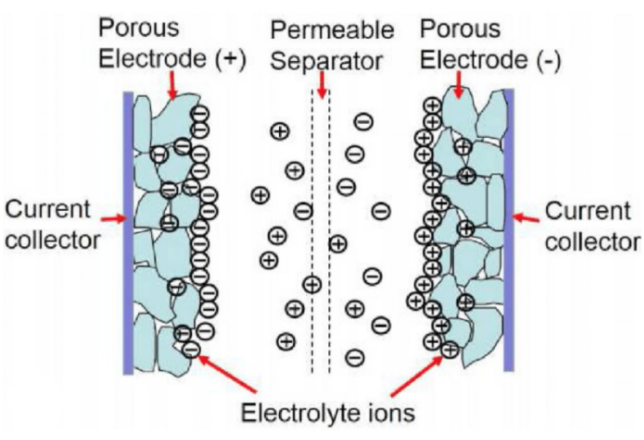

Figure 2.2. EDLC structure (Drummond et al., 2019).

The performance characteristics of an EDLC can be tuned by changing the nature of its electrolyte. In an EDLC, an aqueous or organic electrolyte can be used. Aqueous electrolytes such as H_2SO_4 and KOH generally have lower equivalent series resistance (ESR) and lower minimum pore size compared to organic electrolytes such as acetonitrile. However, aqueous electrolytes have lower breakdown voltages. Therefore, when choosing between an aqueous or organic electrolyte, the balance between capacitance, ESR and voltage must be considered (Frackowiak & Beguin, 2001). While the structure of the electrolyte is of great importance in supercapacitor design, subclasses of EDLCs are primarily distinguished by the form of carbon they use as an electrode material. EDLCs take advantage of the many and frequently cited properties of carbon materials including good chemical stability, good electrical conductivity, availability and low cost (Pandolfo & Hollenkamp, 2006). Carbon materials have long been incorporated into the electrodes of energy storage devices, primarily as electroconductive additives, active ingredient doping, electron transfer catalysts, interlayers, heat transfer, porosity control, surface area, and capacitance. There is an enormous number of carbon materials produced materials ranging from various carbonization and activation procedures and conventional ACs to more complex carbon nanotubes (CNTs) that are being evaluated as electrode materials for EDLCs. The most preferred forms of carbon materials that can be used to store charge in EDLC electrodes are activated carbons, carbon aerogels and carbon nanotubes (Pandolfo & Hollenkamp, 2006; Alonso et al., 2006; Shi, 1996; Portet et al., 2008; Hwang & Hyun, 2004; Kim et al., 2005).

2.2. Pseudocapacitors

While EDLCs store electrostatic charge, pseudocapacitors store charge by reversible redox reactions on the surface of active materials. Since this capacitance is not of electrostatic origin, the prefix "pseudo" is used to distinguish it from electrostatic capacitance. For this reason, the pseudocapacitor's energy storage system is much more complex than that of an EDLC. The separation starts at the electrode surface where a completely different charge storage mechanism is applied, a simple example is given in Figure 2.3.

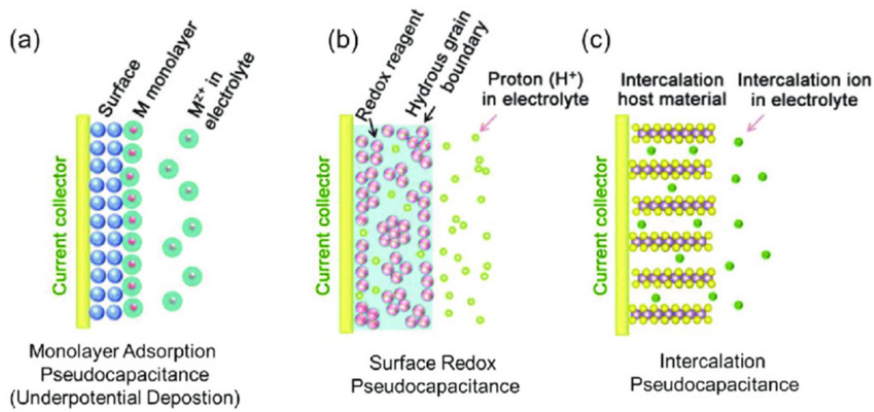

Figure 2.3. Different reversible redox reactions for pseudocapacitors, (a) monolayer adsorption pseudocapacitance, (b) surface redox pseudocapacitance, and (c) intercalation pseudocapacitance (Huang & Niederberger, 2019).

Metal oxide/hydroxides and conductive polymers have mostly been used as electrode materials to store charges in pseudocapacitors (Rudge et al., 1994). Pseudocapacitors involve Faradic redox reactions, and when a potential is applied to the pseudocapacitor, fast and reversible Faradic reactions occur on the electrode materials and produce a charge. Three types of Faradic reactions occur at the electrodes: Reversible adsorption, redox reaction of transition metal oxides/hydroxides, and reversible electrochemical doping-dedoping processes in conductive polymers (Narayanan & Joseph, 2018). Due to these faradaic processes in redox-active materials, a higher capacitance and energy density can be achieved in pseudocapacitors compared to EDLCs. Also, because Faradic processes are slower than non-Faradic processes, pseudocapacitors produce lower power density than EDLC capacitors (Wang et al., 2012). Materials and practical applications of pseudocapacitors are given in the Figure 2.4.

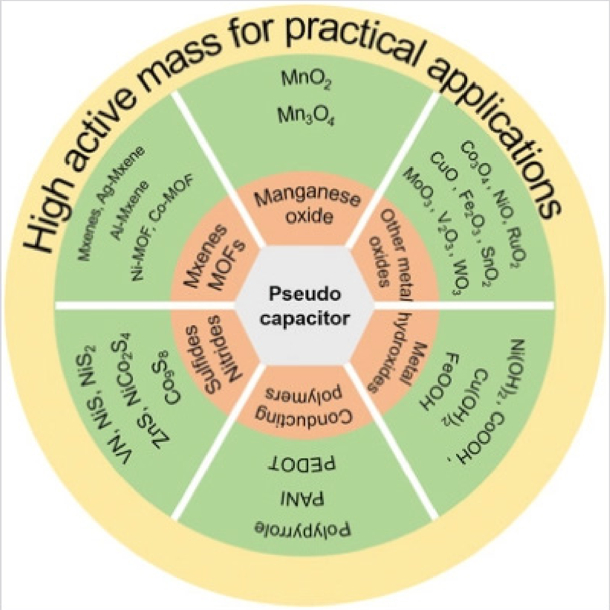

Figure 2.4. Pseudocapacitance materials and applications (Chen et al., 2020).

2.3. Hybrid Supercapacitors

Hybrid electrochemical capacitors consisting of a double-layer carbon material and a pseudocapacitor material have attracted attention recently.

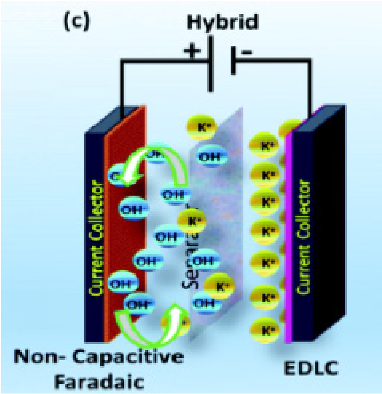

Figure 2.5. Hybrid Supercapacitor (Swain et al., 2021).

The capacitance of hybrid supercapacitors consists of porous carbon materials and double-layer capacitance stored with pseudocapacity stored by metal oxide/hydroxide or conductive polymer (Figure 2.5).

Hybrid capacitors try to take advantage of EDLCs and pseudocapacitors while trying to reduce their disadvantages to achieve better performance characteristics. By using both faradic and non-faradic processes to store charge, hybrid capacitors have achieved greater energy and power densities than EDLCs without the sacrifices in cycle stability and economics that limit the success of pseudocapacitors.

3. Synthesis Methods of Supercapacitor Electrodes

It is necessary to discuss the synthesis processes of electrode materials, which play a very important role in improving the efficiency of the charge-discharge mechanism. These synthesis functions also contribute to controlling the size, surface area and architectures/morphologies of the synthesized electrode materials of nanomaterials (Forouzandeh et al., 2022). Many synthesis methods (Tezel et al., 2022) have been used so far to synthesize supercapacitor materials and has also been given in Figure 3.1.

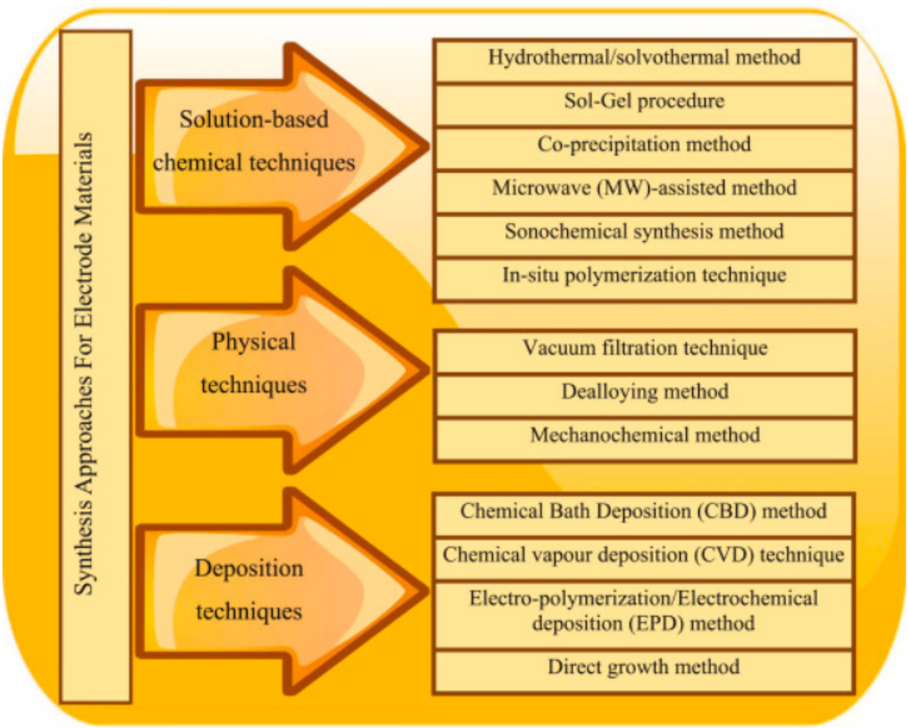

Figure 3.1. Supercapacitor electrode synthesis methods (Forouzandeh et al., 2022).

Some of those; chemical vapor storage (CVD), electrochemical storage, sol-gel, chemical bath storage (CBD) and microwave assisted method (Xia et al., 2011). The most efficient way of electrochemical deposition is the electrodeposition method, which is the production of a thin film on the surface with an electric current. With parameters such as storage speed, film thickness and homogeneity can be controlled and cost-effective (Broughton & Brett, 2005; Reddy & Reddy, 2004; Gomez & Kalu, 2013). CBD is a low temperature technique that allows relatively economical deposition of material on large surface substrates. It involves the direct deposition of the material, which forms a film by the nucleation process, by immersing the substrate in a solution containing different precursors dissolved in both ionic and molecular form without the application of current and voltage. Compared to electrodeposition, the advantages of CBD are that it is relatively inexpensive, simple, suitable for large surface coating, and suitable for low temperature storage (Leela Mohana Reddy et al., 2008; Tezel et al., 2019-a; Tezel et al., 2019-b; Tezel et al., 2021, Tezel and Kariper, 2022). Chemical vapor storage (CVD) is based on the formation of the desired material in the form of a powder or thin film by decomposing of suitable gas molecules on the surface of the substrate with thermal or plasma energy support in a reaction chamber. CVD is often used to synthesize carbon materials, primarily including CNTs and nanofibers (Behm et al., 2013). The sol-gel method is used to synthesize thin film electrode materials for supercapacitors. It is created by surface immersion in a concentrated solution of polymeric or inorganic precursors (Narayanan & Joseph, 2018). The microwave assisted method is an inexpensive, fast and versatile technique (Behm et al., 2013; Antiohos et al., 2013; Fang et al., 2012; Ming et al., 2012). It is well suited for producing narrow size distribution particles and with high purity. High homogeneity, rapid volumetric heating, high yield and controllability over morphology are some of its advantages (Liu et al., 2012; Zhang et al., 2009). In addition, it is remarkable that it shortens the reaction time and improves the nucleation rate in the synthesis of oxide materials in supercapacitor applications (Zhang et al., 2009).

4. Metal Hydroxide Electrode Materials

Metal hydroxides are being developed as electrode materials for use in various fields of supercapacitors, energy and conventional devices. Metal hydroxides exhibit high electrical conductivity and excellent stability over time

(Naeem et al., 2023). Their crystal structure affects their electronic structure. That is, the band gaps and local electron densities affect the redox activity and electron conductivity of the electrodes. 2D interlayered and 1D tunneled crystal structures support bulk diffusion of electrolyte ions, while close-packed crystal structures only support surface redox reactions unless there is a structural change during charge-discharge. When mixed metal oxide and hydroxide metal cations with different ionic diameters combine, they trigger stress-strain, and the change in metal-oxygen bonding in crystals directly affects the redox activity. Amorphous phases facilitate charge transmission reactions due to their weak chemical bonding and increase surface defects. These defects, such as cation and oxygen vacancies, affect electronic structure and redox activity (Nguyen et al., 2023).

Transition metal hydroxides (TMHs) have outstanding potential for the production of supercapacitor electrodes due to their high theoretical capacitance and ultra power density. Energy storages can be achieved either by electrosorption or by reversible redox reactions. Normal valence states change with the charge-discharge function. Therefore, they show greater power density and stability than conventional carbon and conductive polymer materials. Although narrow operating potentials, low conductivity, and small reaction area raise problems, they can be solved by structural engineering and composition, such as dimensional and morphology control (Narayanan & Joseph, 2018). Transition metal hydroxides (TMHs) are widely used for electrochemical applications due to their progressive nanostructured morphological properties. When comparing simple TMHs and binary TMHs, the combination of multiple elements and compounds exhibits great synergistic effects. For example, some types of simple TMHs such as Ni-Co, Fe-Co, and Mo-Co are used in supercapacitors. These binary chemical compounds with different mixed valences affect the redox reaction due to limited conductivity and active states in BTMHs as a result of slow kinetic loading. In addition to BTMHs, ternary TMHs are being developed by combining three metal hydroxides. These TTMHs exhibit high surface area, hierarchical morphologies, numerous active states and multiple covalent states, as a result of enhanced electrochemical activity. For example, triple Zn-Ni-Co nano-arrays show strong supercapacitor performance because Co improves electronic conductivity, Ni provides high capacitance, and Zn transfers electrical conductivity. Fe-Co-Ni triple double-layer hydroxides (DLHs) exhibit strong supercapacitor performance with the impurity Fe improving conductivity leading to the number of active states. There are also MoCoFe-based TTMHs, where

Mo contains various oxidation states (Mo^{5+}, Mo^{3+}), Co is used as catalysis with robust properties and Fe supports excellent conductivity (Nguyen et al., 2023). Ultrathin TMHs have been applied in supercapacitors due to the advantages of their high specific surface area and improved planar electronic conductivity. Most importantly, this atomic thickness further shortens the ion diffusion path and lowers the ion diffusion resistance (Narayanan & Joseph, 2018). Başlıca TMHs Ni, Co, Fe, Mo içeren ikili veya üçlü elektrot yapılardır. The main TMHs are double or ternary electrode structures containing Ni, Co, Fe, Mo.

4.1. Ni Hydroxides

Basically, the structural change of NiOOH electrodes is the increase in their potential range when redox reactions occur. The charging process shortens the Ni-O bands as a result of shifting in the Ni-O stretching vibration and Ni-O bending vibration modes, creating an increase in vibrational polarization to the Ni-O stretching modes after charging. This process is reversible. Changes in oxidation states were noticed at high charge-discharge conditions. Layered NiOOH may contain several cations in the interlayer. Charge storage capacity varies with Ni-O band length, relaxation/slippage of Ni-O vibration, and polarizability (Nguyen & Montemor, 2019).

4.2. Co Hydroxides

$Co(OH)_2$ has been a promising electrode material with its long cycle life, high response rate and high specific capacitance. However, the intrinsic properties and mechanisms underlying good charge storage capacity are still poorly understood. Co valence states changed reversibly after charge-discharge, as evidenced by the same absorption Co K-edge. Some minor adjustments of the atoms occurred, including decreased bond lengths, structural defects during charging, and vice versa during discharge, related to the increased density of Co-O and Co-Co shells and negative shifts. An energy difference occurs in the phase transformation of $Co(OH)_2$ and CoOOH. The activation energies for the phase transformation of $Co(OH)_2$ to CoOOH are 0.76 and 0.34 eV, respectively. This low activation energy, minor structural changes; it can be explained by the high power responsible and the long cycle life of $Co(OH)_2$. During the phase transformation process similar to charge storage in batteries, H^+ deintercalation/intercalation is the result of specific capacity increase (Nguyen & Montemor, 2019).

While $Co(OH)_2$ shows good response rate and cycle life, these properties are generally poor for $Ni(OH)_2$. The good response rate and cycle life of $Co(OH)_2$ platelets is remarkable as its CoO_2 planes are perpendicular to the large area of the platelet, providing a short path for H^+ diffusion for the bulk redox reaction. Moreover, the highly reversible conversion of $Co(OH)_2$/CoOOH prevents morphological breakage as it will change the volume during the H^+ deintercalation/intercalation process. This orientation is probably due to the 3d orbital lined up on octahedral Co^{+2} ions, while $Ni(OH)_2$ is absent in octahedral Ni^{+2}. It is a result of the different orientation of the NiO_2 planes rather than perpendicular to the outer surface of the nanostructures, which slows down the bulk redox process and therefore weakens the response rate and cycle life (Nguyen & Montemor, 2019).

4.3. Fe Hydroxides

Iron oxy hydroxide FeOOH has been studied as the negative electrode in asymmetrical supercapacitors so far, showing pseudocapacitive responsibility in the negative region of the operating potential window in aqueous electrolytes. However, like other hydroxides, the charge storage mechanism of FeOOH is still indistinct and lacks many details. Previously, the study on the charge storage mechanism of nanoplatelet lepidocrocite γ-FeOOH in 1 M Li_2SO_4 was carried out using in situ electrochemistry during the charge-discharge process. These results showed that it is only the shift of Fe K-edge during charging and discharging of the FeOOH electrode, which suggests structural similarity and changes in oxidation state during redox reactions. In octahedral FeO_6, the Fe-O band length decreases when the working potential is increased from -0.8 to 0.1, indicating a change in the Fe oxidation state. Fe-Fe bond lengths also decrease for Fe atoms between adjacent octahedral FeO_6. The charge storage mechanism of FeOOH is explained by considering the relevant valence change in Fe atoms from +2 to +3 during the Li^+ deintercalation/intercalation reaction (Nguyen & Montemor, 2019).

4.4. Mo Hydroxides

Mo plays an important role in tunneling of electronic structures and drawing electrons of active metals, optimizing the adsorption energy of the -OOH group and reducing the barrier energy. Because it has abundant active states (Zhu et al., 2023).

5. Results and Discussion

This study includes discussions and innovations on supercapacitors, their types, advantages and disadvantages, application areas, synthesis methods and metal hydroxide supercapacitor electrode materials. In recent years, significant successes have been achieved in supercapacitor studies and supercapacitor production of companies has increased for various purposes. One of the main reasons for this is a deep understanding of the charge storage mechanism, different electrode engineering ways to enhance electrochemical performance, and the design of flexible and/or smart devices. However, there are still gaps that need to be filled for most research. These gaps will pave the way for new research streams.

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CAHAPTER IX

GAMMA-RAY SHIELDING PARAMETERS FOR PC/$BATIO_3$ COMPOSITES

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1. Introduction

Radiation shields have been essential in safeguarding both humans and the environment against the harmful effects of ionizing radiation. When not adequately shielded, this type of radiation can pose significant risks to human health (Bozkurt, Şahin, Karabul, Kılıç, & Özdemir, 2022; El-Khatib et al., 2022). Lead is the most common shielding material due to its high atomic number and density. However, the use of lead suffers from its toxicity, weight, and lack of flexibility, which led researchers to shift their focus to developing alternative materials for lead. Polymer composites are one of the most important candidates for lead replacement due to their lightweight, flexibility, excellent thermal and chemical stability (El-Khatib et al., 2022). Numerous studies have been conducted to investigate the shielding performance of the polymer composites. For example, Kazemi et al. theoretically investigated gamma radiation shielding performance of PVA/micro and nano WO_3 composites using MCNPX code. The mass attenuation coefficients (MAC) of PVA/50% nanoWO_3 and PVA/50% mikroWO_3 composites were determined as 0.0599 and 0.0532 cm^2/g at 662 keV, respectively (Kazemi & Malekie, 2019). In another study, Mahmoud et al. tested gamma ray shielding performance of HDPE doped nano and micro sized lead oxide (PbO) particles. The findings indicated that the radiation shielding properties were improved with the incorporation of PbO nanoparticles. In addition, nano sized PbO doped composites showed better attenuation performances (Mahmoud et al., 2018).

When the scientific literature is examined, it is seen that polymers that are insufficient in blocking the radiation, are doped with high Z elements to gain attenuation ability. Antimony (Z_{Sb}=51), Barium (Z_{Ba}=56), Cerium (Z_{Ce}=58), Gadolinium (Z_{Gd}=64), Tungsten (Z_W=74), Bismuth (Z_{Bi}=83), are mostly used doping materials due to their high atomic numbers providing superior shielding performance (Almuqrin, ALasali, Sayyed, & Mahmoud, 2023; Bedar et al., 2019; Beyazay, Karabul, Korkut, Kılıç, & Özdemir, 2023; Karabul & İçelli, 2021; Wang et al., 2015). Among these additives, $BaTiO_3$, which is a type of perovskite metal oxide with excellent dielectric, piezoelectric, photoelectric etc. properties, has been studied in only a few studies for gamma radiation shielding despite its high atomic number (F Akman, Kaçal, Almousa, Sayyed, & Polat, 2020; Mhareb et al., 2020). For example, Akman et al. experimentally investigated the radiation shielding performance of Polyester/$BaTiO_3$ and $CaWO_4$ composites. They determined that the radiation shielding properties such as the linear attenuation coefficient, effective atomic number and, radiation protection efficiency increased with the addition of additives (F Akman et al., 2020). In another study, Issa et al. tested the radiation shielding performance of PVA/$BaTiO_3$ composites by using both four different point radioactive sources and FLUKA code. They determined MAC of the composites increased with the amount of $BaTiO_3$ and reached the maximum mass attenuation coefficient as 0.25199 cm^2/g for the composite having maximum $BaTiO_3$ content at 81 keV energy (Issa et al., 2021).

This study aims to investigate the radiation shielding performance of Polycarbonate/$BaTiO_3$ composites with several $BaTiO_3$ concentrations ranging from 5% to 20% by weight. The radiation shielding attributes of the composites were theoretically examined by three parameters such as mass attenuation coefficient, half value layer (HVL), mean free path (MFP) and effective atomic number (Z_{eff}) using both WinXCom software and MCNP6 v.2 simulation.

2. Radiation Shielding Parameters

When a gamma ray penetrates the shielding material, its intensity decreases according to the beer lambert equation (Eq.1.) (Çağlar et al., 2019).

$$I = I_0 e^{-\mu x} \quad (1)$$

where I, I_0 and x represent attenuated photon intensity, incoming photon intensity and the thickness of the shielding material, respectively. The coefficient μ is an important shielding parameter and defined as linear attenuation coefficient. Since the linear attenuation coefficient does not include the density of shielding material, which is one of the most essential factors for the radiation shielding, the mass attenuation coefficient is mostly defined by Equation 2.

$$\mu_m = \frac{\mu}{\rho} (cm^2 g^{-1}) \quad (2)$$

HVL and MFP are other essential shielding parameters, represent the material thickness to reduce incoming radiation to half and the mean distance traveled by a photon between successive collisions, respectively. HVL and MFP are defined by Equation 3 and 4, respectively (Rammah, El-Agwany, Mahmoud, Novatski, & El-Mallawany, 2020; Sayyed, Dong, Tekin, Lakshminarayana, & Mahdi, 2018).

$$HVL = \frac{ln2}{\mu} \quad (3)$$

$$MFP = \frac{1}{\mu} \quad (4)$$

Another crucial parameter to determine radiation protection potential of a sample is effective atomic number, which is the atomic number for multi-element materials. There are several methods to calculate Zeff. Interpolation method is one of these methods and given in Equation 5.

$$Z_{eff} = \frac{Z_1(log\sigma_2 - log\sigma_{eff}) + Z_2(log\sigma_{eff} - log\sigma_1)}{log\sigma_2 - log\sigma_1} \quad (5)$$

Here σ_{eff} is the total atomic cross-section of the material, which can be described by Equation 6. σ_1 and σ_2 represent the cross-section of the lowest and highest value close to σ_{eff}, respectively.

$$\sigma_{eff} = \frac{\left(\frac{\mu}{\rho}\right)_{material}}{N_A \sum \frac{f_i}{A_i}} \quad 6$$

Here f_i and A_i are the molar fraction and the atomic mass of i th element. N_A is Avogadro constant (Kavaz et al., 2019; Rammah et al., 2020).

3. WinXCom and MCNP6

To determine the radiation shielding parameters of the studied sample, both WinXCom software and MCNP6 simulation code were employed. WinXCom is a modified version of XCom software developed by Hubbell and Berger for Windows operating system (Gerward, Guilbert, Jensen, & Levring, 2004). It can calculate the mass attenuation coefficients and cross sections of the shielding materials in the energy range between 1 keV - 100 GeV in accordance with "Mixture Rule" given in Equation 7.

$$\left(\frac{\mu}{\rho}\right)_{material} = \sum_i^n w_i \left(\frac{\mu}{\rho}\right)_i \quad 7$$

Here, $(\mu/\rho)_i$ is MAC value and w_i is the weight of the ith element $(\mu/\rho)_{material}$ represents MAC value of the sample (Kaewkhao, Laopaiboon, & Chewpraditkul, 2008).

MAC values of the composites studied were calculated using WinXCom in the energies between 1 keV - 100 GeV. On the other hand, MAC values of corresponding samples were also calculated by Monte Carlo N-Particle code for several energies between 81-1173 keV. MCNP is a software code for simulating the transport of radiation. It was created by Los Alamos National Laboratory. MCNP6 is the latest version of the Monte Carlo N-Particle code, which is used for simulating the transport of neutrons, electrons, and photons (Goorley et al., 2012; Singh, Medhat, & Shirmardi, 2015; Yasmin, Kamışlıoğlu, & Sayyed, 2023).

Other shielding parameters such as Z_{eff}, MFP and HVL were determined by MAC values obtained by WinXCom and MCNP6 code separately. Table 1 shows the element fractions and densities of PC and PC/$BaTiO_3$ composites used in WinXCom and MCNP6 calculations.

Table 1. The element fractions and densities of PC and PC/$BaTiO_3$

Sample	Element (wt%)					Density (g/cm^3)
	H	C	O	Ti	Ba	
PC	0.06249	0.66196	0.27555			1.2
PC/5% $BaTiO_3$	0.05937	0.62886	0.27206	0.01027	0.02944	1.441
PC/10% $BaTiO_3$	0.05624	0.59576	0.26858	0.02053	0.05889	1.682
PC/15% $BaTiO_3$	0.05312	0.56266	0.26509	0.0308	0.08833	1.923
PC/20% $BaTiO_3$	0.04999	0.52957	0.26161	0.04106	0.11777	2.164

4. Material and Method

MAC values calculated by WinXCom software and MCNP6 simulation code for various energies are given in Table 2.

Table 2. The MAC values of PC and PC/$BaTiO_3$ composites for various energies

Sample	Mass Attenuation Coefficient (cm^2/g) (WinXCom-MCNP6)				
	81 keV	356 keV	662 keV	1173 keV	1332 keV
PC	0.1715-0.1705	0.1061-0.1070	0.0819-0.0816	0.0625-0.0674	0.0585-0.0579
PC/5% $BaTiO_3$	0.2816-0.2995	0.1072-0.1097	0.0816-0.0816	0.0621-0.0615	0.0581-0.0575
PC/10% $BaTiO_3$	0.3917-0.4278	0.1082-0.1124	0.0814-0.0816	0.0617-0.0613	0.0577-0.0574
PC/15% $BaTiO_3$	0.5018-0.5569	0.1092-0.1151	0.0811-0.0817	0.0613-0.0610	0.0573-0.0570
PC/20% $BaTiO_3$	0.6119-0.6847	0.1103-0.1179	0.0808-0.0817	0.0608-0.0604	0.0569-0.0567

To prove the accuracy of MAC values calculated by WinXCom program and MCNP6 code, Relative deviations (RD%) between these results given in Table 2 were calculated according to Equation 8.

$$RD = \frac{\left| MAC^{WinXCom} - MAC^{MCNP6} \right|}{MAC^{WinXCom}} \quad 8$$

The results showed that WinXCom and MCNP6 were in a good agreement with RD between 0.05% and 11.9%. These negligible difference between WinXCom and MCNP6 simulation determined by RD% calculation can be attributed to the mixture rule in WinXCom calculations which does not include the atomic interactions in multi-element materials (Sirin, 2020).

It can be seen from Table 2 that MAC values increased with the increasing of $BaTiO_3$ content and decreased with increase in gamma energy for low energy values. This is because the photon interaction probability decreases with increasing energy and increases with higher $BaTiO_3$ content. All the composites were exhibited higher MAC values than pure PC at low energy values. However, MAC values stayed almost constant at the energies higher than 662 keV, which means the samples could not block high energy radiation. The maximum MAC values were obtained at 81 keV energy, which is the minimum energy level studied in this study. The maximum increase in MAC values was obtained in PC/20% $BaTiO_3$ composite with maximum $BaTiO_3$ content at 81keV. This increase was 3.57 times bigger than pure PC. The increases in MAC values for PC/5% $BaTiO_3$, PC/10% $BaTiO_3$ and PC/15% $BaTiO_3$ composites were 1.64, 2.28 and 2.93 times higher than for pure PC, respectively. Comparing the MAC values of the examined samples with other polymer composite-based shielding materials is important to evaluate their performance. For this purpose, MAC values of composites were compared with other composites in the scientific literature. For example, Kazemi et al. investigated gamma radiation shielding performance of PVA/WO_3 composites by using MCNPX Code. The results revealed that MAC value of PVA/50%wt nanoWO_3 composite at 662 keV is equal to 0.0599 cm^2/g (Kazemi & Malekie, 2019). The MAC value of PC/20%$BaTiO_3$ composite (studied in this study) at 662 keV is 0.0808 cm^2/g. In another study, Akman et al. investigated radiation shielding performance of polyester/lead(II) iodide composites by using HPGe detector and radioactive point sources. They determined that MAC value of PE composite having 20%wt. PbI_2 is 0.6285 cm^2/g at 81 keV (Ferdi Akman et al., 2020). This is quite close to MAC value of PC/20%$BaTiO_3$ at 81 keV.

HVL and MFP values were also computed to assess the radiation protection performance of PC/$BaTiO_3$ composites. Whereas HVL is the material thickness to reduce incoming radiation to half, MFP is the mean distance traveled by a photon between successive collisions. Therefore, the smaller HVL and MFP corresponds better shielding performance. HVL and MFP values of pure PC and PC/BaTiO$_3$ composites at various energies are given in Figure 1.

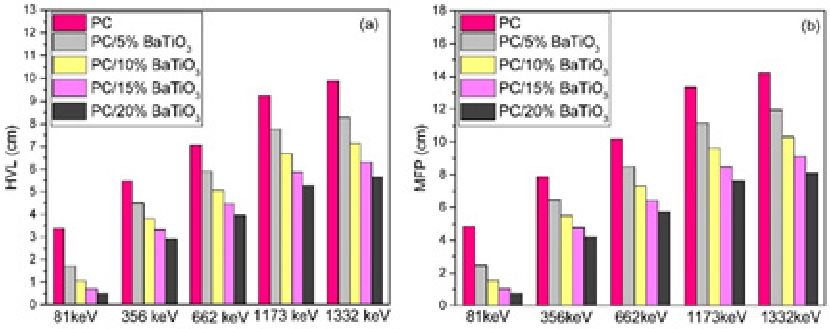

Figure 1. a) HVL, b) MFP values of PC and PC/BaTiO$_3$ composites

According to Fig. 1, HVL and MFP values increase with increasing energy and decrease with BaTiO$_3$ addition. Higher HVL and MFP values mean that gamma photons can penetrate much longer distance in the sample, indicating the sample cannot sufficiently reduce gamma radiation. From this point of view, it can be interpreted that the PC/20% BaTiO$_3$ composite having minimum HVL and MFP values has the best shielding performance in terms of HVL and MFP. On the other hand, HVL and MFP values gradually decrease with the increase of BaTiO$_3$, which means that the shielding performance of composites increases with the incorporation of BaTiO$_3$. While the decreases in HVL values at 81 keV are 1.98, 3.20, 4.69 and 6.43 times for PC/5% BaTiO$_3$, PC/10% BaTiO$_3$, PC/15% BaTiO$_3$ and PC/20% BaTiO$_3$ compared to PC respectively, the decreases in MFP values at 81 keV are 1.97, 3.20, 4.69 and 6.43 times for PC/5% BaTiO$_3$, PC/10% BaTiO$_3$, PC/15% BaTiO$_3$ and PC/20% BaTiO$_3$ compared to PC respectively.

Z_{eff} is an important parameter to investigate radiation shielding performance of any materials. For this purpose, Z_{eff} values of PC and PC/BaTiO$_3$ composites were plotted in Figure 2.

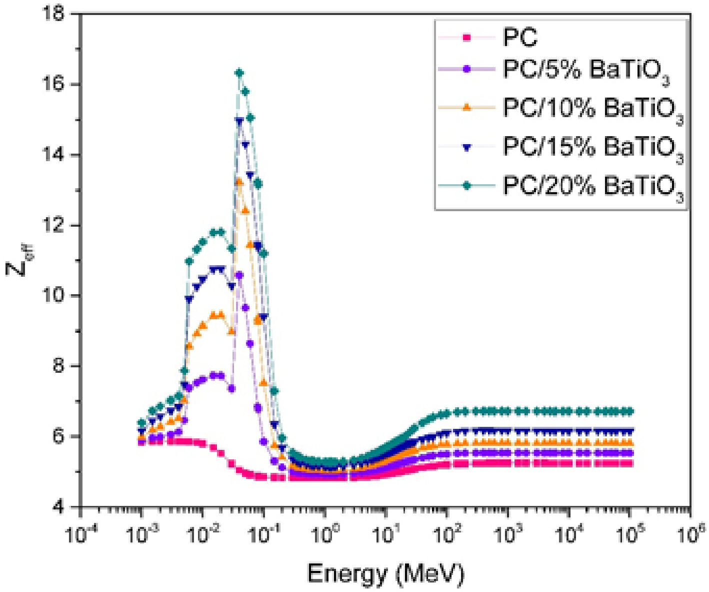

Figure 2. Z_{eff} values of PC and PC/$BaTiO_3$ composites

In Z_{eff} histograms of PC and PC/$BaTiO_3$ composites, three types of photon-matter interaction mechanisms stand out. In the lower energy region, Z_{eff} values are the highest as the photoelectric interaction mechanism is dominant with Z^{4-5} atomic number dependency. Moreover, in this region, Z_{eff} plots of the composites show a small irregular increase corresponding absorption edge of Barium. As the energy rises, Z_{eff} values starts to decrease due to the decrease in dominance of photoelectric interaction and increase in Compton scattering interaction. Then, after this region Z_{eff} increases again due to the interaction mechanism shifts from Compton scattering to pair production. Finally, at high energy region pair production mechanism becomes dominant (Chanthima & Kaewkhao, 2013).

On the other hand, in the composites Z_{eff} values for each photon energy increased with $BaTiO_3$ addition. The maximum Z_{eff} values were obtained in PC/20% $BaTiO_3$ composite, which has the maximum ratios of $BaTiO_3$. This result indicates that PC/20% $BaTiO_3$ composite has best shielding performance among the composites in compatible with MAC, HVL and MFP results.

4. Conclusion

This research focused to examine the gamma radiation protection attributes of PC/$BaTiO_3$ composites as a lightweight, flexible and environmentally friendly option to lead based shielding materials. To achieve this goal, fundamental shielding parameters such as MAC, HVL, MFP and Z_{eff} determined by using WinXCom and MCNP6 simulation code. Relative deviations between WinXCom and MCNP6 calculated between 0.05 and 11.9%. The results revealed that MAC values increased gradually with the addition of $BaTiO_3$ at low energy values. The maximum MAC value was obtained in PC/20% $BaTiO_3$ composite with maximum addition content as 0.612 cm^2/g at 81 keV. The MAC values increased 1.64, 2.28, 2.93 and 3.57 times for PC/5% $BaTiO_3$, PC/10% $BaTiO_3$, PC/15% $BaTiO_3$ and PC/20% $BaTiO_3$ composite compared to PC, respectively. On the other hand, HVL and MFP outcomes showed that HVL and MFP values decreased with the incorporation of $BaTiO_{3,}$ meaning that $BaTiO_3$ improved the shielding ability of the composites. PC/20% $BaTiO_3$ composite exhibited the lowest values for HVL and MFP. Z_{eff} plots depicted characteristic photon-matter interaction mechanisms: photoelectric interaction, Compton scattering and pair production at low, intermediate and high energy regions, respectively. PC/20% $BaTiO_3$ composite had maximum Z_{eff} values for each photon energy. In this context, PC/20% $BaTiO_3$ composite can be recommended as a lightweight, flexible and nontoxic shielding materials for low energy shielding applications.

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CHAPTER X

CREATING A NEW MOBILE APPLICATION SUPPORTED ELECTRONIC CONTROL-TRACKING METHOD FOR OBESITY AND FOOD ALLERGY MONITORING: ARTIFICIAL WILL

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1. Introduction

One of the 10 most risky diseases is obesity according to the World Health Organization (WHO) [Altunkaynak & Özbek, 2006]. Obesity is a disease that occurs as a result of excessive fat accumulation in the body due to reasons such as insufficient physical activity, lack of energy balance, unbalanced and unhealthy eating habits [Kayar & Utku, 2013], imbalance between food intake and energy spent. Such diseases are affecting the whole world day by day thanks to the developing technological devices in daily life and cause serious problems in societies. According to studies, obesity is a health problem that is increasing in prevalence worldwide and causing a great increase in mortality rates [Kalan & Yeşil, 2010]. Obesity often goes hand in hand with cardiovascular disease and life-threatening comorbidities such as type-2 diabetes and some types of cancer [Rutherford, 2010].

In addition to obesity, another problem affecting the daily life of individuals and increasing rapidly due to new generation foods is food allergy. Food allergy usually occurs as a result of abnormal reactions that the immune system develops against some food proteins (profilin, ovalbumin, serum albümin…etc.). In some cases, food allergy may be exacerbated by exercise and this may cause food-related exercise anaphylaxis. Food allergy prevalence is increasing worldwide. Food allergies are more common, especially in children. There is no effective treatment for food allergy. In individuals with allergies, it is recommended to exclude allergen-containing foods from the diet [Tercanlı & Atasever, 2021].

The number of obese individuals and the number of individuals with food allergies are increasing day by day in the population of the country due to the changing nutritional structures. Some people are aware and aware of this situation and take precautions. On the other hand, some people are not aware of this situation and live openly to threats. Taking motivation from this information, it is necessary to work on the subject of obesity and food allergy with a technological solution and follow-up focus.

In the literature, besides the studies examining the effects of obesity, many technological studies have been carried out for the prevention and treatment of obesity. Some of these studies are: Focused on obesity solutions based on knowledge management, devices and materials in [Rutherford, 2010]. Information is given about signal devices for monitoring, implantable and wearable devices developed based on biomedical engineering. They have designed a method to help facilitate health management via a smartphone associated with radio frequency identification (RFID) in [Chen & Shi, 2012]. The two main functions of the designed system are drug reminders and drug identification. In [Bouharati et al., 2012], the fuzzy logic-based structures were supported by artificial intelligence (AI), and a configuration was created to prevent the emergence of obesity according to the conditions in the system inputs. The device has been developed to track and monitor the food consumption of individuals in [United States Patent, 2017]. In the related study, there is a sensor that can be incorporated into wearable technologies that automatically collects data for the detection of eating events. This product, which can be integrated with smart wristbands and mobile phones, monitors the chemicals in the food content. In [Mohammed et al., 2018], it is aimed to follow-up patients with wearable technology. It is purposed to encourage a healthy eating culture and adopt a lifestyle with physical activity, thanks to smartphones and wearable devices that provide obesity control and follow-up. In addition, a new smart system proposal has been presented alongside the existing systems. In [Akıncı et al., 2022], a study has been conducted to compare and select wearable technologies to be used in remote monitoring of obesity patients. In the evaluation of wearable technologies for obesity patients, inactivity warning, water drinking monitoring, water resistance, battery life, charging time, and price criteria have been effective in product selection. In the related study, multi-criteria decision-making methods have been preferred to ensure obesity monitoring by encouraging the user to move and regulating their eating habits thanks to wearable technologies.

In this study, which accepts the information in the literature and the lack of health in the field of engineering-based technologies as a source of motivation, an electronic artificial will (AW) is created. Because the solutions offered need to take an active part in the daily life of individuals. Although the "ingredients" part of packaged products is written on the foods consumed to meet the nutritional needs of individuals, most individuals cannot find time to read it while shopping. In addition, it is not possible to know how much the substances in it are used and whether there are any side effects on the health of the individual during shopping. The existence of problems such as the existence of a lot of information pollution, the fact that most weight control applications provide services based on 'general' information, pushes people into confusion and uncontrolled actions occur. In line with all these developments and information, it is important that individuals follow the foods with obesity and allergy effects by using technological opportunities. Thanks to the electronic control-tracking system created in this study, the calorie amounts of packaged foods and the substances they contain are associated with a barcode. Thanks to this system and the mobile application (M-APP) developed together with it, it is ensured that the purchasing situation for packaged products in online shopping and grocery shopping is completed in a healthy way for the individual. In case of exceeding the limit values, the will of the individual is warned by giving a warning by the system.

2. Method and Materials

It is ensured that the purchasing situation for packaged products is completed in a healthy way for the individual, as in Figure-1, in online shopping, grocery shopping, pharmacy shopping and dietitian service recommended consumption, thanks to the electronic tracking-control system and M-APP designed in this study. Control card activation is completed in line with the information that individuals enter into the application. This data, obtained by calculating the body mass index (BMI) of individuals, is transferred into the card. The definition of BMI developed by the WHO to determine obesity is: It is expressed in kg/m^2 by proportioning the weight of individuals to their heights. The amount of calories that an individual can consume daily, monthly or yearly can be seen on the card, which is read to the barcode readers in the markets during shopping. The first security level of the healthy shopping phase is completed by automatically reducing the calorie amount of the purchased product from the daily calorie amount of the individual or individuals. At the same time, in serious ailments that require more specific and nutritional control, the characteristics and contents of the products purchased before the person's shopping is completed, and the second safety stage is passed. The shopping process is completed successfully after the second safety stage, the allergy active substance screening, is passed. In addition, the products purchased can be tracked by selecting the appropriate categories from the mobile phone application. By reading the barcode/QR of the purchased product, the curious nutrients in the product can be seen. In this way, it can be examined whether the purchased product contains substances that trigger effects such as allergic reactions and food intolerances. Due to this advantageous feature, it is ensured that possible disease triggering factors that are overlooked for individuals are minimized. On the other hand, it is aimed to reduce the increasing obesity situations by controlling it by AW.

Management cards such as STM32, Raspberry Pi [Yüzgeç & Aba, 2017], Odroid XU, Banana Pi, Rock, Orange Pi, UDOO Bolty, LattePanda Alpha & Delta, Omega2Plus, NVIDIA Jetson [Valladares, 2021; Shin & Kim, 2022], Arduino have been researched in line with the mentioned aims and objectives [URL-1, 2023]. Raspberry Pi and Arduino board have been chosen respect to accessibility, cost, and functionality. As seen in Figure-2, Arduino card has been preferred among the two alternatives and has been used as the management unit of the study. The system detailed in Figure-3 has been prepared with the "master-slave" layout. Arduino and ESP32 are masters, and LCD, RC522, barcode reader are considered as slaves in system.

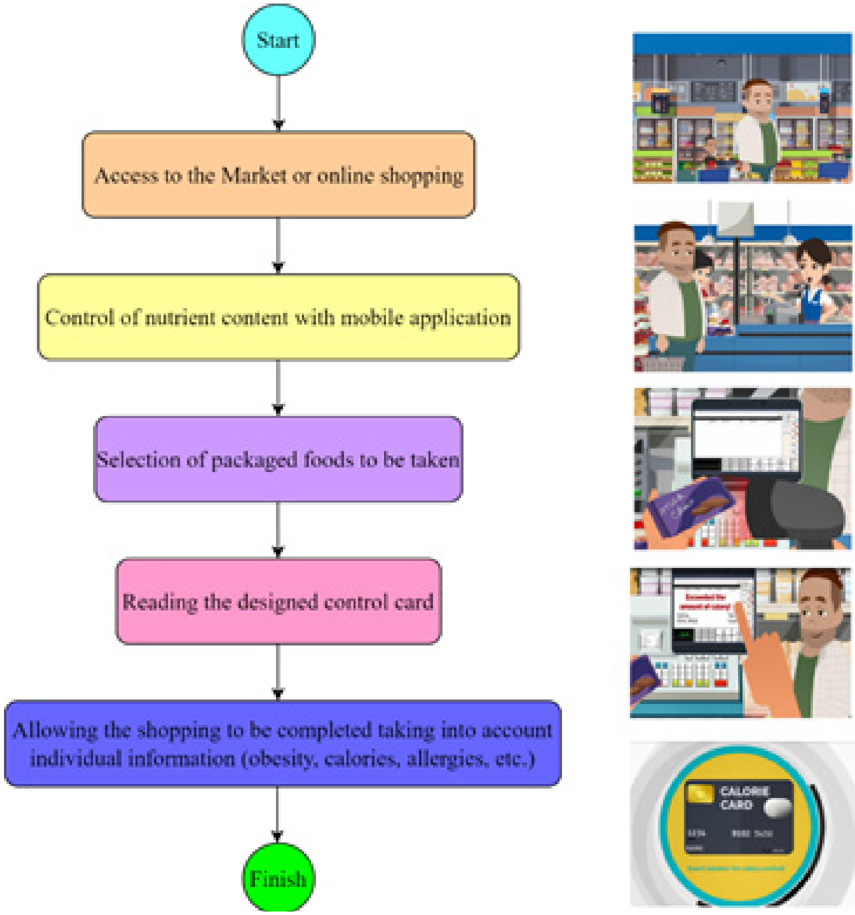

Figure 1. Controlled shopping processes and flowchart

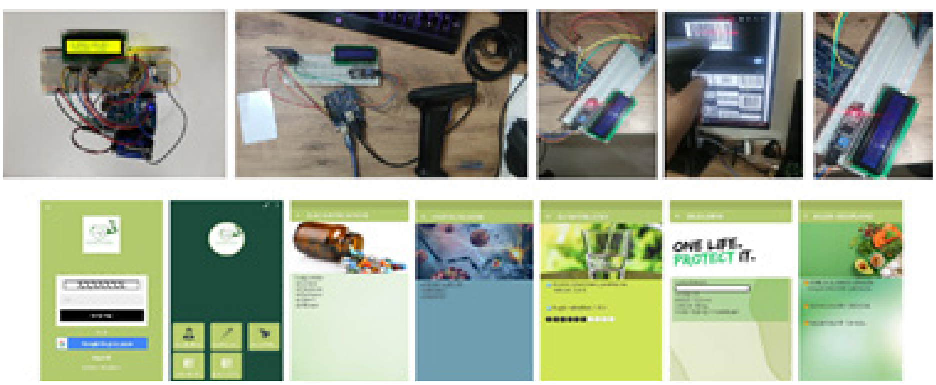

Figure 2. Development of a mobile application supported electronic tracking-control system

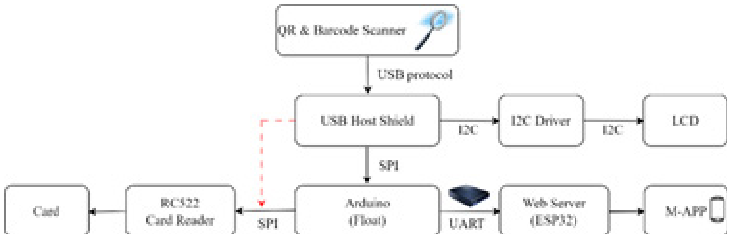

Figure 3. “Master-slave” layout and installation diagram of the system

To complete a basic exchange, a healthy communication between the Arduino board and the communication module (Wi-Fi ESP32) is ensured. Various types of communication are used in the system. With the RF technology, computer network issues are processed, data exchange is made on the card and communication between the sensors is ensured with serial communication. The steps for the synchronous and stable operation of the master-slave units, communication units and M-APP in the installed system are as follows:

Step 1. Communication of USB protocol with USB hostshield connected to Arduino board,

Step 2. Reading the product barcodes related to the barcode reader,

Step 3. The read data is sent to USB hostshield and transferred to Arduino board via SPI (serial peripheral interface) communication,

Step 4. Checking the incoming data and detecting the read product,

Step 5. Communication is established between the LCD and Arduino via I2C (inter-integrated circuit) serial communication,

Step 6. Writing the caloric value of the product, which is determined by selecting from the list defined in the data store of the system, to the LCD screen (The product information read on the LCD side, the calories of the product and the calories of the total products read are included.)

Step 7. Reading the desired products to the RC522 card module (There is adjustable balance/fund data in the card.),

Step 8. Subtracting the read balance from the total calorie balance,

Step 9. In case the card’s balance is not sufficient, “insufficient balance/fund” warning is given (Fund can be loaded via a button or the loading system.),

Step 10. If the relevant card is not defined, giving the “unidentified card” warning,

Step 11. After the card is read and the balance changes, a UART communication starts between the second master, ESP32, and Arduino.

Step 12. Updating the balance in the account defined to the card via the server created via ESP32 with the card.

Step 13. The balance on the card defined to the server carrying M-APP data can be tracked synchronously with M-APP.

There are important points to be considered in the M-APP part, which can synchronize with electronic units: It is important that the application be functional and that it can be designed in a way that users of all ages can easily understand.

3. Conclusion and Discussion

In this study, an artificial will (mobile application supported electronic tracking-control system) has been created to provide obesity control, calorie control, and protection from allergy-active substances based on food tracking, and a prototype product has been created by following the needs of the society. After passing certain safety and preventive steps, the purchasing situation for products such as packaged food and medicine is completed in a healthy way for the individual, thanks to the prototype product. The daily, monthly or yearly calorie amount of the individual can be seen on the card read by the individual at the shopping place and in the system. BMI and the individual's needs are taken into account to calculate this amount. The calorie amount of the purchased product is reduced from the calorie amount that the user can take daily, allowing for healthy shopping. In addition, it is checked whether the ingredients in the purchased products are an allergy-active substance for the individual. Alternatively, the amount of sugar that should be taken for diabetics can also be followed. In the product supported by the mobile application, different categories can be selected and medication, reminders, calories, diabetes, allergies, and the amount of drinking water can be tracked.

Thanks to the prototype product created in the study, it is aimed to increase the living standards of individuals who struggle with obesity, adopt a healthy life, have a certain food allergy or have a food-related disease that needs attention, and lead a healthier life. To achieve this goal, it is aimed to gain an artificial will by using a smart filtering system about the contents of foods.

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CHAPTER XI

FEMALE ACADEMICS IN EARTH SCIENCE: THE CASE OF TURKEY

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1. Introduction

Gender is to culturally define and differentiate material bodies coded by biology by attributing spiritual meanings to them. It is to identify women and men with the totality of roles and statuses called femininity and masculinity. This distinction plays a leading role in the emergence of many inequalities to the detriment of women. It is known that discussions on gender and discrimination started in the 1960s. It is observed that the concepts of gender and biological sex in these discussions are sometimes confused with each other. Gender-based discrimination is characterised on the basis of associating women's gender with their biological sex and narrowing, preventing or prohibiting the tasks, jobs and professions that women can undertake. In the social sciences literature, two different concepts of gender, biological and social gender, are discussed. While biological gender is the classification of individuals as men and women according to their physical characteristics, social gender defines the different roles and behaviours of men and women in society. Gender is a socially constructed phenomenon. Within this phenomenon, certain personality or other social characteristics are referred to as masculine or feminine, and are wrongly assumed to arise spontaneously from having a male or female body. Equality between women and men is an issue that should be emphasised in the field of education as in all areas of society. According to the World Health Organization, sex refers to the biological and physiological characteristics that define women and men, while gender refers to the socially constructed roles, behaviours, activities and qualities that a society deems appropriate for women or men (Özkanlı and Korkmaz, 2000; Bingöl, 2014; Başarır and Sarı, 2015; Yıldız, 2018; WHO, 2018).

Women are involved in production activities with various forms of work in every period and society. The variety in women's forms of work gives the concept of work a different meaning and content for men and women. The fact that women's "working" does not only consist of economically productive activities makes participation in working life and working conditions different for women and men. As in many other areas of public life, women's inclusion in the field of education and scientific production has been realised step by step through long years of struggle. In different countries, women's ability to work as scientists at universities did not happen all at once; women were first able to follow courses at universities and were admitted as students to certain departments, and later all departments at universities accepted women students. Depending on the development of the struggles in their countries, women first started university education in some countries with co-education; in others, women and men students who initially studied separately became co-educated over time. There are still countries in the world where co-education at university level is prohibited and/or women are admitted only to certain departments. It was only in the years following their admission as university students that women were able to work as scientists at universities (Özçatal, 2011; Şentürk, 2015).

It is generally accepted that the process of women's participation in the history of universities in Turkey has some differences from the Western European and Anglo-Saxon world. As part of the modernisation process, the emergence of the university institution in Turkey was accompanied from the very beginning by the reform process regarding women's education. Therefore, universities, as visible institutions of modernisation and westernisation, became one of the institutions that symbolised the regime's ideals of modern women and were shaped by the participation of women from the very beginning. In every modern society there are assumptions about a certain, correct and desirable form of gender relations and gender division of labour. It cannot be said that the functioning of the university as an institution is not affected by the dynamics of the society in which it is shaped, and the gender regime. Universities are expected to be outside of gender debates due to their institutional identities and missions. However, studies and the facts reflected in the numbers show that this social problem also has a counterpart at the university level (Öztan and Doğan, 2015; Şentürk, 2015, Karakuş, 2016).

Today, when education is recognised as one of the fundamental rights, the time spent in education has increased compared to the past, and women's demands for access to higher education and advancement in academic careers have also increased. With the presence of women academics in scientific life, the responsibilities imposed on women in working life have also increased. On the basis of gender, it is not possible to evaluate women's household production, which is expressed as invisible labour, in terms of labour-value. On the other hand, the obligations of being an academic in working life have also increased the burden on women performing this profession. In order to understand women's presence in academic life in positions at the lower rungs of the hierarchy and in departments related to professions deemed "appropriate" for women, it is necessary to understand women's relations with work, family and private lives. The activities required for a career in academics, such as publishing articles, attending congresses and supervising dissertations, extend beyond working hours and require sacrifices from private life (Dikmen and Maden, 2012; Küçükşen and Kaya, 2016; Adak, 2018).

Another reflection of gender in the academy is the observation of a distinction between men and women at the level of sciences. Accordingly, the general opinion is that human-oriented social sciences are suitable for women and data-oriented science is suitable for men. The studies conducted in Turkey have findings to support that science is masculine and social sciences are feminine. The existence of a gendered segregation at the level of sciences in academic fields cannot be ignored. Although we are living in an age where many scientific innovations and important discoveries have been made, women working in academic fields still face some difficulties in advancing their careers and realising their scientific studies. Due to the difficulties experienced, women have a very narrow field of work in the world of science and can contribute very limitedly (Yıldız, 2018; Demir, 2018).

In the academy, which is almost completely dominated by men, it is seen that women are gradually beginning to gain a place for themselves. In fact, in certain fields such as nursing, education and social service, women are in the majority both as students and faculty members. However, some research shows that women are still under-represented in male-dominated disciplines such as science, medicine, law or literature due to gender and sex-discriminatory perspectives. Over the past 30 years, women in the western world have taken important steps towards academia. Many barriers that prevented women from participating in higher education have been broken down. In the 1932-1933 academic year, women started to work as academics at universities in Turkey with the recruitment of women as lecturers at the Higher School of Economics and Commerce (Skelton, 2005; Hirshfield and Joseph, 2012; Şentürk et al., 2017).

With the development of technology, knowledge and control over technology has created a new area of power in society. Engineering fields, which are based on technology, have become male-dominated. It is assumed that engineering is characterised by neutral, logical, pragmatic, aggressive and competitive qualities that are associated with masculine qualities and are inherently incompatible with female characteristics. Over the last 20 years, the number of female students in earth sciences and related engineering programmes has increased significantly in Turkey. For the distribution of female faculty in many fields at universities in Turkey, gender distribution for female students in engineering is also available. The highest percentage of female faculties is in chemistry, biology, food and environmental sciences, and there is also a notable increase in fields related to earth sciences. Although the percentage of women faculty is higher in Turkey, the data show that women are still underrepresented in the earth sciences (Okay, 2003; Okay, 2007; Emre, 2007; Okay, 2008).

In this study, the entrance of women as academics to universities in Turkey where Mining, Geology, Geophysics and Petroleum and Natural Gas Engineering education is provided, their academic career processes and the conditions of gaining a place in academia in these departments, which are considered to be male-dominated in society, are examined by making use of national and international literature. The main purpose of the study is to examine where women academics in earth sciences departments are in the academy, their presence in the academy, and to offer solutions based on the inequality in the ratio of women/men.

2. The Aim, the Importance and Method of the Study

The careers of women academics continue to be a focus of gender studies, as women often have different career paths from their male counterparts and are still underrepresented at senior levels. Gender bias is a major obstacle in academia as women, their ideas and findings are underestimated. Moreover, the male-dominated academia makes it very difficult for women academics to climb the career ladder. Accordingly, gender-based segregation in academia is analysed under two headings: horizontal and vertical. While gender-based segregation of scientific fields is defined as horizontal segregation, hierarchical segregation is defined as vertical segregation. According to the 2023 statistical data of the Council of Higher Education (CHE), the proportion of female academics in all universities in Turkey is 44.7% in faculties of Medicine, 43.9% in departments of Mathematics, 90.6% in departments of Nursing and 14.3% in departments of Mechanical Engineering; the rate of female academics in all universities in Turkey is 46.2%; the rate of female professors is 33.9%; the rate of female associate professors is 40.8%; the rate of female assistant professors is 46.6%, the rate of female lecturers is 51.5% and the rate of female research assistants is 53.2% (HEIMS, 2023). As can be seen from this table, the ratio of female academics in the departments of nursing and mechanical engineering is an example of horizontal segregation, while the difference in the range from professor to research assistant is an example of vertical segregation. As women progress in academic career processes, they lose approximately 20 per cent until they reach the title of professor.

Another problem women face in academia is the difficulties they experience in advancing in their professions. The glass ceiling is a popular metaphor used to explain the inability of many women to progress beyond a certain point in their professions and jobs, regardless of their qualifications or achievements. Women keep struggling to achieve equality in the workplace and are repeatedly hitting their heads against the glass ceiling. Many women never even get close to the glass ceiling due to gender bias. The "maternal wall" that prevents women from advancing after becoming a mother and the sharp impact of having children on their careers is an undeniable fact. Nevertheless, several reasons have been put forward for the glass ceiling effect: overt gender discrimination, traditional division of housework and childcare responsibilities, incompatibility of family and professional roles, gender differences in lifestyle preferences, self-selection, women's lower self-esteem, less support from family, supervisor and colleagues, gender stereotyping, sexism, disregard for gender differences and bias in recruitment and selection procedures. While many of the barriers mentioned are likely to have been faced by female academics, the fact that they have actually broken through the glass ceiling may mean that they have found ways to cope or neglect it (Purcell et al., 2010; Jones and Palmer, 2011; Williams, 2005; Willemsen and Millar, 2009).

In the academic world, a considerable number of women academics remain in low-level positions and experience difficulties in academic progress, even though they have established their presence for many years. The "pump-priming" hypothesis that upward mobility in the professional hierarchies would happen naturally once access had been secured did not materialise and reality contradicted expectations. Women academics are being lost at every step. This loss, known as the "leaky pipeline", has long been a matter of concern in the field of science and technology. There is an aspect of negativity in the use of this metaphor, implying that leakage, like leaks in pipes, is a total absence. It is correct that women are poorly represented in high-level academic roles. However, it is also important to recognise that the choice to pursue a career in science is always a personal choice and should take into account individuals' circumstances, abilities and ambitions (Etzkowitz and Ranga, 2011; Rasmini, 2016).

In recent years, the inclusion of women in working life has increased both in the world and in Turkey compared to the past years, and has gained more importance than in the past due to social changes. It is very important to be a female academic, to be able to exist in academia, and to be able to identify and take action against the negativities that female academics face/may face; especially in departments that are considered to be male-dominated, such as Mining, Geological, Geophysical, Petroleum and Natural Gas Engineering, which are considered as earth sciences engineering. This study was conducted on male and female academics employed in universities with Mining Engineering, Geophysical Engineering, Geological Engineering and Petroleum and Natural Gas Engineering departments. In the first part of the study, a detailed literature research has been carried out. In this context, the concepts of gender and gender-based discrimination were given and women's entry into working life, women's entry into university and academia were analysed. Finally, with the advancement of technology, the position of women in the academy in earth sciences was mentioned. The second part of the study consists of female academics currently employed in earth science engineering departments in Turkey. In this context, the distribution of academics by title and gender was given. In the light of the data obtained, where women academics were in the academy and their presence in the academy were analysed, and solution suggestions were presented based on the inequality in the ratio of women/men.

3. Results

The distribution of male and female academics in 24 universities with Mining Engineering departments in Turkey by title and gender is given in Table 1.

Table 1: Title and Gender-based Distribution of Academics in the Department of Mining Engineering (CHE Academic, 2023).

	Professor				**Associate Professor**				**Assistant Professor**				**Lecturer**				**Research Assistant**				**Final Total**			
Name of the coll.	**M**	**F**	**T**	**F (%)**	**M**	**F**	**T**	**F (%)**	**M**	**F**	**T**	**F (%)**	**M**	**F**	**T**	**F (%)**	**M**	**F**	**T**	**F (%)**	**M**	**F**	**T**	**F (%)**
ATU	3	0	3	0,0	0	0	0	0,0	2	0	2	0,0	0	0	0	0,0	1	1	2	50,0	6	1	7	14,3
AKU	4	0	4	0,0	4	0	4	0,0	1	1	2	50,0	2	0	2	0,0	1	0	1	0,0	12	1	13	7,7
AU	1	0	1	0,0	1	0	1	0,0	0	0	0	0,0	0	0	0	0,0	1	0	1	0,0	3	0	3	0,0
COMU	1	0	1	0,0	0	1	1	100,0	2	0	2	0,0	0	0	0	0,0	0	0	0	0,0	3	1	4	25,0
CU	7	1	8	12,5	1	0	1	0,0	1	2	3	66,7	0	0	0	0,0	1	1	2	50,0	10	4	14	28,6
DU	7	2	9	22,2	0	0	0	0,0	2	0	2	0,0	1	0	1	0,0	0	1	1	100,0	10	3	13	23,1
DEU	17	0	17	0,0	6	3	9	33,3	2	0	2	0,0	1	0	1	0,0	5	3	8	37,5	31	6	37	16,2
ESOGU	13	2	15	13,3	2	2	4	50,0	5	0	5	0,0	0	0	0	0,0	1	4	5	80,0	21	8	29	27,6
GSU	0	0	0	0,0	2	0	2	0,0	1	0	1	0,0	0	0	0	0,0	4	0	4	0,0	7	0	7	0,0
HU	8	1	9	11,1	5	2	7	28,6	5	1	6	16,7	0	1	1	100,0	6	2	8	25,0	24	7	31	22,6
ITU[1]	8	0	8	0,0	3	1	4	25,0	1	0	1	0,0	0	0	0	0,0	7	1	8	12,5	19	2	21	9,5
ITU[2]	6	2	8	25,0	1	1	2	50,0	3	0	3	0,0	0	0	0	0,0	3	6	9	66,7	13	9	22	40,9
INU	4	0	4	0,0	2	1	3	33,3	0	0	0	0,0	0	0	0	0,0	0	0	0	0,0	6	1	7	14,3
IU-C	4	2	6	33,3	6	0	6	0,0	3	0	3	0,0	1	0	1	0,0	2	2	4	50,0	16	4	20	20,0
KTU	10	1	11	9,1	5	0	5	0,0	0	0	0	0,0	0	0	0	0,0	5	1	6	16,7	20	2	22	9,1
KTUN	7	1	8	12,5	2	1	3	33,3	2	0	2	0,0	0	0	0	0,0	6	1	7	14,3	17	3	20	15,0
DPU	9	2	11	18,2	1	0	1	0,0	5	0	5	0,0	0	0	0	0,0	2	1	3	33,3	17	3	20	15,0
MSKU	3	0	3	0,0	3	1	4	25,0	0	0	0	0,0	0	1	1	100,0	1	0	1	0,0	7	2	9	22,2
OHU	2	0	2	0,0	3	1	4	25,0	1	1	2	50,0	0	0	0	0,0	0	0	0	0,0	6	2	8	25,0
METU	2	1	3	33,3	1	0	1	0,0	2	0	2	0,0	0	0	0	0,0	5	5	10	50,0	10	6	16	37,5
SDU	8	0	8	0,0	2	0	2	0,0	1	0	1	0,0	0	0	0	0,0	1	2	3	66,7	12	2	14	14,3
SU	2	0	2	0,0	0	1	1	100,0	3	1	4	25,0	0	0	0	0,0	0	0	0	0,0	5	2	7	28,6
UU	2	0	2	0,0	0	0	0	0,0	2	0	2	0,0	0	0	0	0,0	0	0	0	0,0	4	0	4	0,0
YYU	1	0	1	0,0	2	1	3	33,3	4	2	6	33,3	0	0	0	0,0	1	0	1	0,0	8	3	11	27,3
BEUN	7	0	7	0,0	2	0	2	0,0	3	0	3	0,0	0	0	0	0,0	2	0	2	0,0	14	0	14	0,0
Total	**136**	**15**	**151**	**9,9**	**54**	**16**	**70**	**22,9**	**51**	**8**	**59**	**13,6**	**5**	**2**	**7**	**28,6**	**55**	**31**	**86**	**36,1**	**301**	**72**	**373**	**19,3**

ITU[1]: Mining Engineering Department
ITU[2]: Mineral Processing Engineering Department

A total of 55 male research assistants, 5 male lecturers, 51 male assistant professors, 54 male associate professors and 136 male professors are employed in 24 universities, while the number of female research assistants is 31, female lecturers is 2, female assistant professors is 8, female associate professors is 16 and female professors is 15. In Mining Engineering departments, 36.1% of research assistants, 28.6% of lecturers, 13.6% of assistant professors, 22.9% of associate professors and 9.9% of professors are women. While there are 72 female academics in all universities, this number is 301 for male academics and based on these data, the ratio of female academics in Mining Engineering departments in Turkey is 19.3%. When the data are analysed, it is seen that it is compatible with the "leaky pipeline" theory and "glass ceiling" theory. As women move up academically, they endanger.

The distribution of male and female academics in 12 universities with Geophysical Engineering departments by title and gender is given in Table 2.

Table 2: Title and Gender-based Distribution of Academics in the Department of Geophysical Engineering (CHE Academic, 2023).

	Professor				**Associate Professor**				**Assistant Professor**				**Lecturer**				**Research Assistant**				**Final Total**			
Name of the coll.	**M**	**F**	**T**	**F (%)**	**M**	**F**	**T**	**F (%)**	**M**	**F**	**T**	**F (%)**	**M**	**F**	**T**	**F (%)**	**M**	**F**	**T**	**F (%)**	**M**	**F**	**T**	**F (%)**
AU	5	1	6	16,7	1	0	1	0,0	2	1	3	33,3	0	0	0	0,0	1	1	2	50,0	9	3	12	25,0
COMU	3	0	3	0,0	2	0	2	0,0	1	2	3	66,7	0	0	0	0,0	0	1	1	100,0	6	3	9	33,3
DEU	4	3	7	42,9	3	3	6	50,0	3	1	4	25,0	3	0	3	0,0	3	2	5	40,0	16	9	25	36,0
GSU	2	0	2	0,0	0	0	0	0,0	0	1	1	100,0	1	0	1	0,0	1	2	3	66,7	4	3	7	42,9
ITU	4	3	7	42,9	2	2	4	50,0	3	0	3	0,0	0	0	0	0,0	5	3	8	37,5	14	8	22	36,4
IU-C	8	1	9	11,1	2	2	4	50,0	2	5	7	71,4	0	0	0	0,0	3	5	8	62,5	15	13	28	46,4
KTU	3	2	5	40,0	4	0	4	0,0	2	1	3	33,3	0	0	0	0,0	0	2	2	100,0	9	5	14	35,7
KOU	3	1	4	25,0	3	1	4	25,0	1	0	1	0,0	1	0	1	0,0	2	0	2	0,0	10	3	13	23,1
SAU	1	0	1	0,0	0	0	0	0,0	7	0	7	0,0	0	0	0	0,0	2	0	2	0,0	10	0	10	0,0
SCU	1	0	1	0,0	0	0	0	0,0	0	1	1	100,0	1	0	1	0,0	1	0	1	0,0	4	1	5	20,0
SDU	7	0	7	0,0	2	0	2	0,0	0	0	0	0,0	1	0	1	0,0	2	3	5	60,0	12	3	15	20,0
YYU	0	0	0	0,0	2	1	3	33,3	1	0	1	0,0	0	0	0	0,0	0	0	0	0,0	3	1	4	25,0
Total	**41**	**11**	**52**	**21,2**	**21**	**9**	**30**	**30,0**	**22**	**12**	**34**	**35,3**	**7**	**0**	**7**	**0,0**	**20**	**19**	**39**	**48,7**	**112**	**52**	**164**	**31,7**

A total of 20 male research assistants, 7 male lecturers, 22 male assistant professors, 21 male associate professors and 41 male professors were employed in 12 universities, while the number of female research assistants was 19, the number of female assistant professors was 12, the number of female associate professors was 9 and the number of female professors was 11. In Geophysical Engineering departments, 48.7% of research assistants, 35.3% of assistant professors, 30.0% of associate professors and 21.2% of professors are women. While there are 52 female academics in all universities, this number is 112 for male academics. Based on these statistics, the rate of female academics in Geophysical Engineering departments in Turkey is 31.7%. When the results are examined, it is seen that it is in compliance with the “leaky pipeline” and “glass ceiling” theory. As women move up academically, their numbers decrease. However, when considering the rates of female academics, it is promising that these rates are relatively close to the rates of male academics.

The distribution of female and male academics in 33 universities with Geological Engineering departments by title and gender is given in Table 3.

Table 3: Title and Gender-based Distribution of Academics in the Department of Geological Engineering (CHE Academic, 2023).

	Professor				Associate Professor				Assistant Professor				Lecturer				Research Assistant				Final Total			
Name of the coll.	M	F	T	F (%)	M	F	T	F (%)	M	F	T	F (%)	M	F	T	F (%)	M	F	T	F (%)	M	F	T	F (%)
AKU	2	0	2	0,0	1	0	1	0,0	1	2	3	66,7	0	0	0	0	1	0	1	0,0	5	2	7	28,6
AKDU	4	2	6	33,3	1	0	1	0,0	1	2	3	66,7	0	1	1	100,0	3	1	4	25,0	9	6	15	40,0
ASU	1	1	2	50,0	1	0	1	0,0	4	0	4	0,0	1	0	1	0,0	1	1	2	50,0	8	2	10	20,0
AU	10	1	11	9,1	2	3	5	60,0	0	0	0	0,0	1	1	2	50,0	2	2	4	50,0	15	7	22	31,8
BAUN	4	0	4	0,0	3	0	3	0,0	3	0	3	0,0	1	0	1	0,0	2	1	3	33,3	13	1	14	7,1
BATU	0	0	0	0,0	0	0	0	0,0	2	0	2	0,0	0	0	0	0,0	2	1	3	33,3	4	1	5	20,0
COMU	3	0	3	0,0	1	1	2	50,0	0	2	2	100,0	0	0	0	0,0	0	0	0	0,0	4	3	7	42,9
CU	6	3	9	33,3	3	0	3	0,0	0	1	1	100,0	0	0	0	0,0	4	3	7	42,9	13	7	20	35,0
DEU	14	1	15	6,7	6	2	8	25,0	2	2	4	50,0	0	1	1	100,0	5	3	8	37,5	27	9	36	25,0
ESOGU	6	0	6	0,0	0	1	1	100,0	1	1	2	50,0	0	0	0	0,0	1	3	4	75,0	8	5	13	38,5
FU	4	5	9	55,6	1	3	4	75,0	3	2	5	40,0	0	0	0	0,0	7	7	14	50,0	15	17	32	53,1
GSU	2	2	4	50,0	6	0	6	0,0	0	0	0	0,0	1	0	1	0,0	2	1	3	33,3	11	3	14	21,4
HU	15	1	16	6,3	6	2	8	25,0	3	1	4	25,0	0	3	3	100,0	7	6	13	46,2	31	13	44	29,5
ITU	16	5	21	23,8	4	0	4	0,0	5	5	10	50,0	1	2	3	66,7	11	8	19	42,1	37	20	57	35,1
IU-C	7	2	9	22,2	2	0	2	0,0	3	2	5	40,0	0	1	1	100,0	8	6	14	46,2	20	11	31	35,5
KSU	2	1	3	33,3	1	0	1	0,0	1	1	2	50,0	0	0	0	0,0	0	0	0	0,0	4	2	6	33,3
KTU	12	5	17	29,4	0	1	1	100,0	2	2	4	50,0	2	0	2	0,0	2	1	3	33,3	18	9	27	33,3
KAEU	0	0	0	0,0	1	0	1	0,0	0	2	2	100,0	0	0	0	0,0	0	1	1	100,0	1	3	4	75,0
KOU	5	0	5	0,0	5	0	5	0,0	2	1	3	33,3	1	0	1	0,0	1	3	4	75,0	14	4	18	22,2
KTUN	10	2	12	16,7	6	1	7	14,3	4	3	7	42,9	0	0	0	0,0	5	1	6	16,7	25	7	32	21,9
DPU	5	0	5	0,0	0	1	1	100,0	6	3	9	33,3	0	0	0	0,0	0	1	1	100,0	11	5	16	31,3
MEU	6	2	8	25,0	1	1	2	50,0	1	2	3	66,7	0	0	0	0,0	0	0	0	0,0	8	5	13	38,5
MSKU	3	1	4	25,0	2	1	3	33,3	1	1	2	50,0	0	1	1	100,0	4	2	6	33,3	10	6	16	37,5
NEVU	2	1	3	33,3	0	1	1	100,0	2	0	2	0,0	0	0	0	0,0	1	0	1	0,0	5	2	7	28,6
OHU	3	0	3	0,0	3	0	3	0,0	5	1	6	16,7	0	0	0	0,0	0	1	1	100,0	11	2	13	15,4
METU	8	1	9	11,1	4	1	5	20,0	1	0	1	0,0	0	0	0	0,0	8	6	14	42,9	21	8	29	27,6
PAU	9	3	12	25,0	9	0	9	0,0	1	1	2	50,0	0	0	0	0,0	1	0	1	0,0	20	4	24	16,7
RTEU	1	0	1	0,0	1	1	2	50,0	0	0	0	0,0	0	0	0	0,0	0	0	0	0,0	2	1	3	33,3
SCU	5	1	6	16,7	2	0	2	0,0	4	0	4	0,0	0	0	0	0,0	2	1	3	33,3	13	2	15	13,3
SDU	4	1	5	20,0	3	3	6	50,0	2	3	5	60,0	0	0	0	0,0	0	1	1	100,0	9	8	17	47,1
YYU	2	0	2	0,0	5	3	8	37,5	3	6	9	66,7	0	0	0	0,0	0	0	0	0,0	10	9	19	47,4
YOBU	2	1	3	33,3	0	3	3	100,0	0	1	1	100,0	0	0	0	0,0	0	0	0	0,0	2	5	7	71,4
BEUN	0	1	1	100,0	0	0	0	0,0	1	0	1	0,0	0	0	0	0,0	2	2	4	50,0	3	3	6	50,0
Total	**173**	**43**	**216**	**19,9**	**80**	**29**	**109**	**26,6**	**64**	**47**	**111**	**42,3**	**8**	**10**	**18**	**55,6**	**82**	**63**	**145**	**43,5**	**407**	**192**	**599**	**32,1**

A total of 82 male research assistants, 8 male lecturers, 64 male assistant professors, 80 male associate professors and 173 male professors were employed in 33 universities. The number of female research assistants is 63, the number of female lecturers is 10, the number of female assistant professors is 47, the number of female associate professors is 29 and the number of female professors is 43. In the Geological Engineering departments of 33 universities in Turkey, 43.5% of research assistants, 55.6% of lecturers, 42.3% of assistant professors, 26.6% of associate professors and 19.9% of professors are women. A total of 192 female academics work in all universities, while the number of male academics is 407, and based on these numbers, the ratio of female academics in Geological Engineering departments in Turkey is 32.1%. When the findings are investigated, it is seen that they are in line with the "leaky pipeline" and "glass ceiling" theory. Women are losing ground as they rise academically. However, when we look at the percentage of female academics, it is encouraging that these rates are relatively close to the male academician rates.

The title and gender-based distribution of male and female academics in 5 universities with Petroleum and Natural Gas Engineering departments is given in Table 4.

Table 4: Title and Gender-based Distribution of Academics in the Department of Petroleum and Natural Gas Engineering (CHE Academic, 2023).

	Professor				Associate Professor				Assistant Professor				Lecturer				Research Assistant				Final Total			
Name of the coll.	M	F	T	F (%)	M	F	T	F (%)	M	F	T	F (%)	M	F	T	F (%)	M	F	T	F (%)	M	F	T	F (%)
BATU	1	1	2	50,0	2	0	2	0,0	2	3	5	60,0	0	0	0	0,0	2	0	2	0,0	7	4	11	36,4
ISTE	4	0	4	0,0	0	0	0	0,0	1	2	3	66,7	0	0	0	0,0	2	0	2	0,0	7	2	9	22,2
ITU	2	0	2	0,0	3	0	3	0,0	3	2	5	40,0	0	1	1	100,0	4	1	5	20,0	12	4	16	25,0
IKCU	2	0	2	0,0	0	0	0	0,0	2	1	3	33,3	0	0	0	0,0	2	1	3	33,3	6	2	8	25,0
METU	3	0	3	0,0	1	0	1	0,0	2	1	3	33,3	0	0	0	0,0	8	2	10	20,0	12	4	16	25,0
Total	**12**	**1**	**13**	**7,7**	**6**	**0**	**6**	**0,0**	**10**	**9**	**19**	**47,4**	**0**	**1**	**1**	**100,0**	**18**	**4**	**22**	**18,2**	**44**	**16**	**60**	**26,7**

A total of 18 male research assistants, 10 male doctoral lecturers, 6 male associate professors and 12 male professors were employed in 5 universities, while the number of female research assistants was 4, the number of female lecturers was 1, the number of female assistant professors was 9 and the number of female professors was 1. In Petroleum and Natural Gas Engineering departments of 5 universities in Turkey, 18.2% of research assistants, 100.0% of lecturers, 47.4% of assistant professors and 7.7% of professors are women. While there are 16 female academics in all universities, this number is 44 for male academics and according to these values, the ratio of female academics in Petroleum and Natural Gas Engineering departments in Turkey is 26.7%. In Figure 1, the title-based ratios of female academics employed in Earth Sciences engineering are graphised.

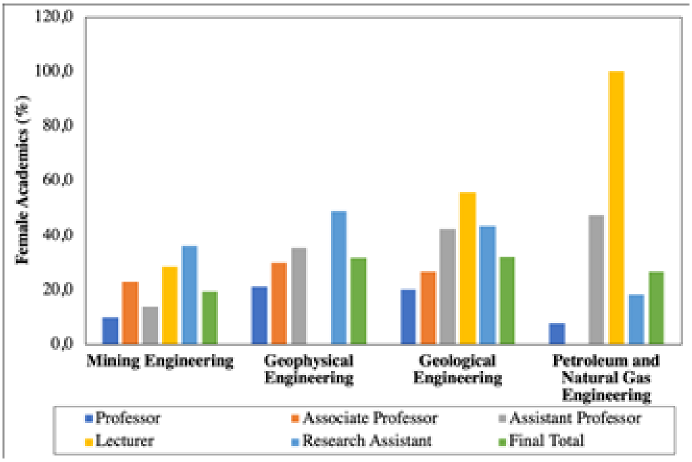

Figure 1: The Title-based Ratios of Female Academics Employed in Earth Sciences Engineering

Considering the studies conducted in other countries on female earth sciences academics, the situation is seen against women, as is the case in Turkey, as shown in Figure 1 (Fru et al, 2021; Mosuro et al., 2023; Pereira and Diaz, 2016; Brink and Stobbe, 2009; Imber et al., 2017). Wherever they are in the world, it is evident that women in academia, especially in male-dominated departments such as earth sciences, are still trying to overcome glass ceilings by breaking them with their hands, and are making a lot of effort to avoid leaking through the hole pipes.

4. Conclusions

The fact that women are more involved in academia today than in the past is very pleasing due to the contribution of women to the development of science. Not only in Turkey but also in the world, women's entrance to higher education and academia has increased over the years. In addition to these positive achievements, it is observed that the representation of women in the academy is still not at an adequate level in departments that are labelled as "male-dominated". However, this situation is not unique to Turkey, but is also observed in developed Western societies. In the world, engineering departments still have the lowest number of female academics. Although in some engineering departments such as chemistry and environmental sciences, the balance of male/female academics seems to be relatively balanced, in many engineering departments the scales are tipped in favour of the masculine side. The general perception of Earth Sciences Engineering is that it is a "male-dominated" profession. For this reason, even at the very beginning of higher education entrance, female students prefer these departments much less than male students. When the data obtained from this study are analysed, it is seen that the presence of women in the "research assistant" staff, which is the first step of entry into academia, is approaching that of male research assistants. Although this result is quite hopeful, it is observed that the representation rate of women starts to decrease as the academic level increases. It is observed that the representation rate of women starts to decline from assistant professorship, which is the next step after research assistantship. When the previous studies on the presence of women in academia are analysed, the general perception is that women have problems in remaining loyal to academia. Although there are various reasons for this, one of the most recognised reasons is the fact that the desire to be in the community overrides the idea of progress. Of course, in addition to this, due to the roles of "woman" and "man" constructed by the society, women's responsibilities in home life as well as work life may hinder women's academic career progress. Since Earth Sciences Engineering, like many other engineering departments, is a professional group that has a body load as well as a brain load, academicians do not have the chance to work independently from the place in their researches, projects and scientific publications by utilising experimental study data. This brings with it the necessity to go beyond the classical working hours. The fact that women generally prefer conformism in working life and prioritise family life brings along the necessity of making a choice after a while in academic progress, especially in engineering departments. The following suggestions can be offered for the continuation of women's academic processes in Earth Science Engineering:

- The first step to be taken is undoubtedly to provide detailed information about Earth Sciences engineering before entering higher education and to ensure that women get rid of the prejudice that these departments are male-dominated departments.
- Among the female engineer candidates studying in these departments, those who are considering an academic career should be encouraged, and they should be included in academic studies by academics by giving them various tasks while they are still students. In this way, they can have the opportunity to recognise and understand the concept of academics.

- Additional studies should be carried out for female research assistants to determine their career progression and career goals. In this way, the idea of continuity in the profession can be instilled in young academics.
- Again, female research assistants can be given different responsibilities in which they can use their initiatives and experience where they will be in the academy in the future. In this way, a transition phase and adaptation process can be initiated for the responsibilities they will have in the future.
- Female research assistants should be given the awareness that they should follow the agenda and technological developments both in their own departments and in other disciplines, be aware of innovations and constantly update their knowledge. In this way, it can be ensured that academics start to be seen as a "profession" rather than a "job".

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CHAPTER XII

INVESTIGATION OF THE PERFORMANCES OF DDK AND GAUSS FILTERING TECHNIQUES IN ELIMINATION OF MODEL-BASED ERRORS

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1. Introduction

Changes in the earth's gravity field can be observed thanks to the GRACE satellites, which began to operate in 2002 (Doğanalp, 2013; Liu, 2008). Until 2017, GRACE satellites successfully fulfilled their mission. Since 2018, GRACE Follow-On (GRACE-FO) satellites have continued to operate (Loomis, Croteau, Sabaka, Luthcke, & Rachlin, 2020). GRACE and GRACE-FO satellites broadcast three sets of data, Level-1, Level-2, and Level-3 (Fischer, 2017). Level-1 data is published as Level-1A product and Level-1B product. Level-1A products are raw data collected from satellites, calibrated, and containing time information. Expert-level knowledge is required for the use of these products. Level-1B products consist of filtered distance information and ancillary data such as acceleration measurement and can be used for specific targets such as earthquake investigations (S. C. Han, Sauber, & Pollitz, 2014; Yuan, 2018). Level-2 data is used in approximately monthly gravity field estimates and orbital solutions for satellites, which are published in the form of spherical harmonic coefficients. Level-3 data transforms monthly gravity anomalies in Level-2 data into surface mass anomalies and provides gridded data. Level-3 grids are updated as Level-2 data becomes available (Dahle et al., 2019).

The spherical harmonic coefficients published by GRACE/GRACE-FO cannot be used directly in calculating geopotential variations. Calculations can be made by eliminating model-based errors with the help of a model created from long-term averages or static models (Godah, 2019; Godah, Szelachowska, & Krynski, 2015). In studies with GRACE/GRACE-FO, calculations are made mainly by creating an average model since a long-term time series has been formed since 2002. The mentioned models cannot completely eliminate the error effects on the coefficients. Because of these errors, reducing the noise seen at higher-order coefficients is necessary. There are various filter methods used for this purpose. The isotropic method, which depends only on the harmonic degree. The anisotropic method, which depends on both the harmonic degree and order and the optimal filter methods depending on the signal variances and measurement errors, are examples of these methods (Seo & Wilson, 2005; Swenson & Wahr, 2002). The most used method in GRACE/GRACE-FO applications is the Gaussian smoothing filter, which is an isotropic method. A disadvantage of the Gaussian filter is that it is insufficient for local studies that require high resolution. If the smoothing radius is kept small in order to preserve the short wavelength information, bands are seen systematically in the north-south line in the relevant spatial region. The reason for this is the correlations between the harmonic coefficients (Swenson & Wahr, 2002). In order to eliminate these effects, the radius of the filter can be increased. If the filter radius is increased, there will be a loss in signal and resolution. In place of preventing these situations, additional correlation filtering techniques can be applied. Among the methods developed for this purpose, the DDK filtering method is among the most preferred methods (Atlı, 2022).

DDK filtering methods are offered to users by data centers. No extra smoothing or decorrelation operations are required for DDK filters published in different radius from 1 to 8. As mentioned above, the filter radius is inversely proportional to the resolution. That is, as the radius increases, the resolution decreases. A precise filter method is not mentioned in line with the studies conducted with GRACE/GRACE-FO. Preferred filters may differ according to the relevant field in which the user works. Filter selection aims to minimize other errors without losing the resolution and signal in geopotential changes (Atlı, 2022).

In the study, firstly, model-based errors in GRACE/GRACE-FO Level-2 data with spherical harmonic coefficient expansion published by different data centers were tried to be eliminated. To eliminate these errors, a long-term average model was created first. Annual average values obtained from Level-2 data published monthly were subtracted from the average model produced, and some model-related errors were corrected. However, DDK filters with different radius and Gaussian filters are needed to eliminate the correlation effects completely. Both filter techniques were applied to the model, and the results were examined. While choosing the radius of the Gaussian filters, the radius approximately equivalent to the DDK filters is selected. Thus, two different filtering models could be compared.

No model-based errors affecting the accuracy were encountered in the maps obtained as a result of the long-term average model created with the Level-2 data obtained from the CSR data center. Gaussian and DDK filter techniques were applied to eliminate the correlation effects. However, long-term average models created with Level-2 data from GFZ and JPL data centers show errors impairing accuracy. These errors were eliminated thanks to the submodel created with the DDK3 filtered solution, which was ideally selected from the CSR data center results. JPL and GFZ mean models were extracted from the generated CSR DDK3 mean submodel, and model-based errors in JPL and GFZ data were corrected. After the model-based errors were eliminated, Gaussian and DDK filters were applied to the JPL and GFZ data to reduce the correlation effects.

2. GRACE/GRACE-FO Satellite Systems

GRACE satellites, which started to work as a result of the joint work between NASA and GFZ in 2002, consist of two satellites that follow each other with a distance of 220±50 km, unlike other satellites. After more than 15 years in service, the GRACE satellites were able to capture temporal changes in the Earth’s gravity field and provided datasets for analysis. GRACE, which has successfully completed its role in monitoring the changes in the Earth’s gravitational field, has left its place to the GRACE-FO satellites (Atayer, 2012; Atlı, 2022; Holfmann & Moritz, 2006).

GRACE and GRACE-FO broadcast the data monthly continuously through three different processing centers.

- JPL (Jet Propulsion Laboratory)
- GFZ (GeoforschungsZentrum Potsdam)
- CSR (Center for Space Research at University of Texas, Austin)

Earth gravity fields from the GRACE and GRACE-FO satellites are officially generated at two levels (Level-1 and Level-2). This data system is generated by the Science Data System (SDS) and broadcasted between SDS, CSR, JPL, and GFZ (Doorn Brad, Jasinski Michael, Reager J T, & Margaret, 2016).

Level-2 data is used in approximately monthly gravity field estimates and orbital solutions for satellites, which are broadcasted in the form of spherical harmonic coefficients (Dahle et al., 2019).

3. Gaussian Smoothing Filter

GRACE and GRACE-FO satellites offer monthly gravity field solutions with harmonic coefficients that expand to a certain degree and order. However, due to some error sources, noise is observed in high-order, that is, short-wavelength coefficients. As the degree of solution increases, the noise level also increases (Simav, 2012; John Wahr, Molenaar, & Bryan, 1998; John Wahr, Swenson, & Velicogna, 2006).

Although a certain degree of termination of the coefficients is offered as a solution, it is not considered the preferred method when considering spatial resolution and truncation error (John Wahr et al., 2006). Instead of this method, spatial smoothing, filtering of potential coefficients, and regional average are preferred in order to obtain a more suitable signal-to-noise ratio (Simav, 2012).

Although many methods have been presented for the spatial smoothing technique, the easiest and most common method is Gaussian smoothing or spatial Gaussian filter (Chen, Wilson, & Seo, 2006; John Wahr et al., 1998).

In the harmonic unfolding equations in geopotential changes, the process of cutting the series sums in a specific place $(n = n_T)$ is called truncation. In addition, coefficients after the relevant degree are not taken into account. This operation is described by a weight function (W_n^*) of n order.

$$W_n^* = \begin{cases} 1, & for\, n < n_T \\ 0, & for\, n \geq n_T \end{cases} \tag{1}$$

This generated function is scaled by the surface harmonic variation $(\Delta Y_n(\vartheta, \lambda)))$. The surface harmonic is scaled as

$$\Delta\bar{Y}_n(\vartheta,\lambda) = W_n^* \Delta Y_n(\vartheta,\lambda)$$
$$= \sum_{m=0}^{n} (\Delta C_{nm} cosm\lambda + \Delta S_{nm} sinm\lambda) W_n^* P_{nm}\ (cos\vartheta) \qquad (2)$$

With the filtering, the standard deviation of the change decreases while the accuracy increases. When this function is applied, the change signals are more or less mixed with each other. In order to avoid this situation, the Gaussian weight function is used, and this function is defined iteratively (van der Wal, Wu, Sideris, & Shum, 2008; J Wahr, 2007).

$$W_n = \begin{cases} 1 & , for\ n = 0 \\ [(1+e^{-2b})/(1-e^{-2b}) - 1/b] & , for\ n = 1 \\ \left[-\frac{2n+1}{b}\right] W_{n-1} + W_{n-2} & , for\ n \geq 2 \end{cases} \qquad (3)$$

The coefficient *b* given here is a function of the smoothing radius R.

$$b = \frac{\ln(2)}{1 - \cos\ (R/a)} \qquad (4)$$

When the Gaussian weight function (W_n) is applied to the surface harmonic variation,

$$\Delta\bar{Y}_n(\vartheta,\lambda) = W_n \Delta Y_n(\vartheta,\lambda)$$
$$= \sum_{m=0}^{n} (\Delta C_{nm} cosm\lambda + \Delta S_{nm} sinm\lambda) W_n P_{nm}\ (cos\vartheta) \qquad (5)$$

equality is filtered out. This filter called the isotropic filter, depends only on the n-order. Anisotropic filters are defined as filters that rely on both the *n* order and the *m* order (S.-C. Han et al., 2005).

In GRACE/GRACE-FO applications, the filter length (R), which is generally preferred in the 300-1000 km range, is an arbitrary value. As the filter size increases, the weight function approaches 0 towards more minor degrees. In other words, higher-order coefficients representing the short wavelength of the signal are disabled in the solution. However, as the errors decrease, the solutions' standard deviations will decrease. When the filter size is reduced, the short wavelength signal at the higher order coefficients of the signal is preserved, thus increasing the resolution. However, significant amplitude errors in higher-order coefficients become more evident in the solution and cause a decrease in accuracy (Atayer, 2012; Kusche, 2007).

Standard filter sizes are out of the question when working with GRACE/GRACE-FO. As the size of the working area gets smaller, the filter size needs to be reduced to bring the resolution to an adequate level. However, it should not be forgotten that solutions will be subject to disruptive effects. For this reason, filtering can be applied by trial and error method to create a balance between resolution and accuracy, depending on the region's size to be studied (Atayer, 2012; Kusche, 2007).

4. DDK Filters

The Decorrelation Filter (DDK) filtering method differs from Gaussian filters in that, in addition to being an anisotropic method, it uses approximate coefficient errors, a complete matrix of covariance errors, and normalized values of spherical harmonics. A kernel function ensures that errors due to the orbital path are eliminated by azimuth-weighted coefficients (narrower in the north-south direction, more comprehensive in the east-west direction). The spectrum of a given filter was generated as a result of experimental mathematical modeling of the error covariance matrix and methods of developing Level 1 to 2 observations based on distance measurements between GRACE satellites using a K-band intersatellite sensor (Szabó & Marjańska, 2020).

Users can access time series through the International Center For Global Earth Models (ICGEM) data center by taking GRACE/GRACE-FO Level-2 harmonic coefficients raw and applying the Gaussian filtering method or using DDK-filtered solutions directly (Ince et al., 2019). DDK solutions are produced for eight different filter radius. These solutions are DDK1, DDK2, DDK3, DDK4, DDK5, DDK6, DDK7 and DDK8. DDK filter radius corresponds approximately to some Gaussian radius. For example, DDK1 filter corresponds to 530 km, DDK2 filter 340 km, DDK3 filter corresponds to Gaussian filtering with a radius of 240 km (Flechtner, Sneeuw, & Schuh, 2014; Güneş, 2018).

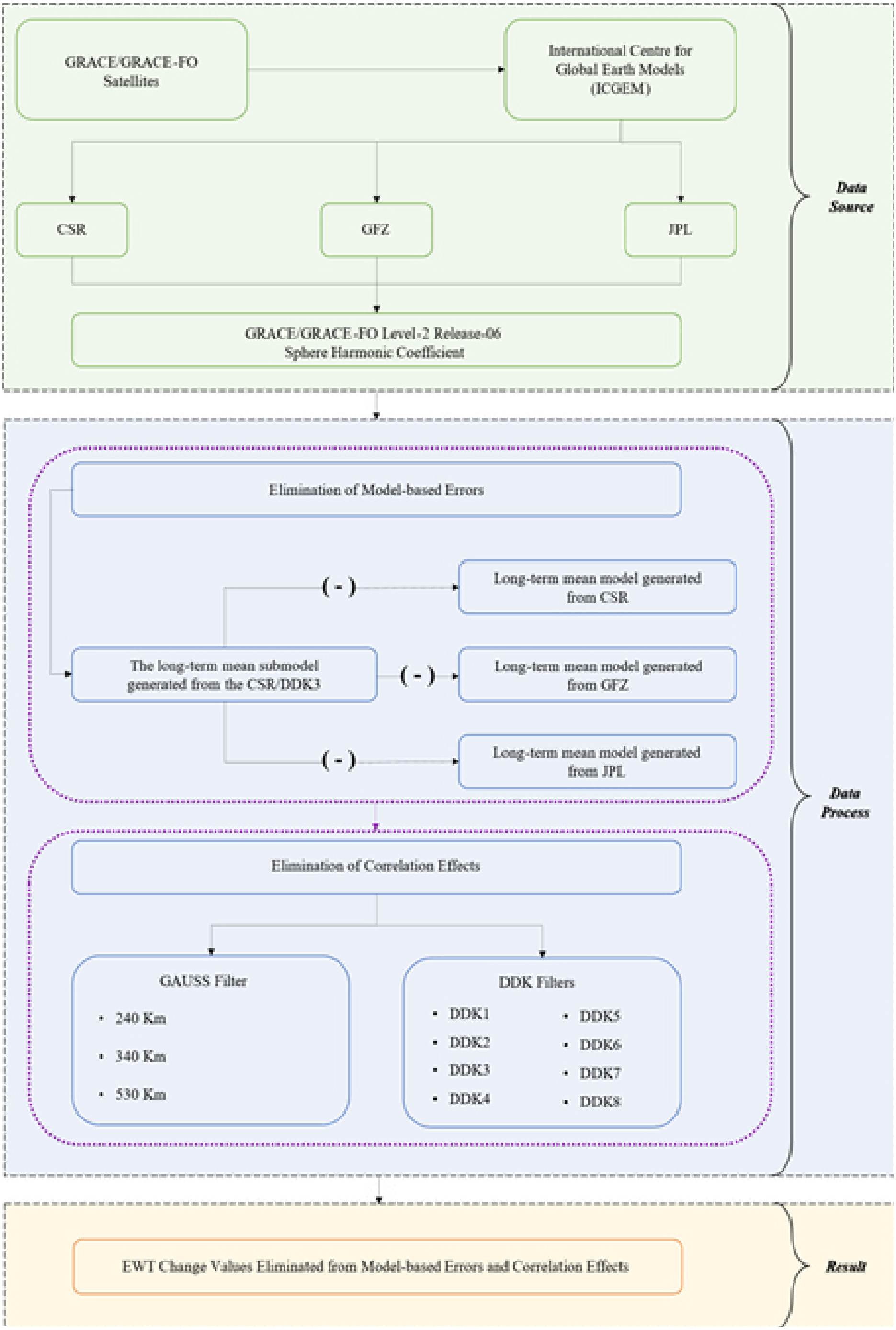

Figure 1. The Workflow schema of the study

5. Comparison of Different Data Centers and Filtering Techniques

GFZ, CSR, and JPL data centers publish GRACE/GRACE-FO Level-2 Version-06 data in the same format. However, the data is not loaded with precisely the same errors and correlations. Therefore, different filters may be considered appropriate for each data center. In order to determine the proper filters, DDK filters and Gaussian filters with different radius were applied separately to the solutions obtained from each data center. The aim is to keep the signal losses to a minimum while eliminating the correlation effects.

The DDK filters applied for the data received from the CSR data center are given in Figure 2. The figure shows the effects of the decorrelated DDK filters on the EWT changes for 2008. When we look at the DDK1 and DDK2 filters, it is seen that the said errors and correlations are eliminated to a high extent, but the signals are subject to smoothing too much. This somewhat confuses data accuracy. The DDK3 data showed that the correlation effect was slightly higher than the DDK1 and DDK2 filters, but the signals were not lost excessively. In the DDK4, DDK5, DDK6, DDK7, and DDK8 filters, it is seen that the stripes increase gradually in the north-south direction and affect the signal accuracy.

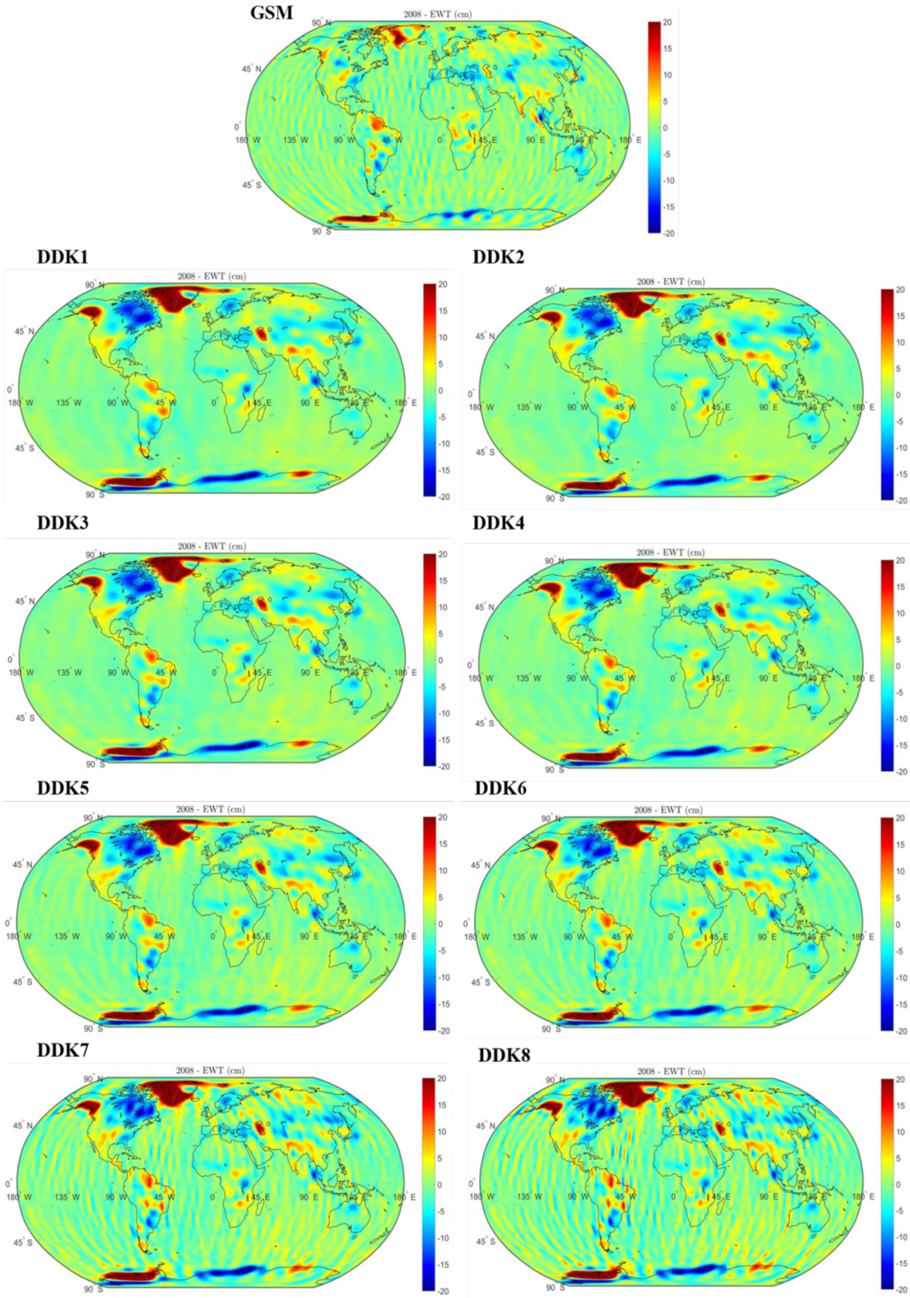

Figure 2. Comparison of CSR GRACE/GRACE-FO Level-2 Version-06 data with raw data (GSM) and DDK filters over EWT solutions

The DDK filters applied on the EWT solutions created with the data received from the GFZ data center are given in Figure 3. In the solutions obtained from the long-term average model created with the GFZ data, it was observed that there were distortions in the poles and equator (Figure 3). Although appropriate filtering techniques were applied to the solutions obtained as a result of the average model obtained from the GFZ data covering the 2002-2021 period, the errors could not be eliminated. Therefore, a submodel was needed. It was observed that the errors in the GFZ solutions obtained by subtracting the average of the sub-model created with the CSR DDK3 data were eliminated (Figure 4).

Looking at the DDK filters applied for GFZ data solutions, it is seen that the DDK1 and DDK2 filters mostly eliminate correlation effects and errors but also mix signal effects. Correlation effects are seen in the DDK3 filter, albeit slightly. However, the rate of mixing signals and reducing accuracy is lower than DDK1 and DDK2. Using the DDK3 filter in the solutions of the GFZ data center has been deemed appropriate.

Before the data obtained from the JPL data center were processed, the data files were edited. There are missing degrees in the harmonic coefficient expansion of some monthly data. Therefore, the data solutions for these months are laden with errors. Figure 5 shows the DDK filters applied to JPL data solutions. Like other data centers, JPL data is laden with correlations and errors. In addition, when the JPL data were analyzed by taking the mean model within itself, as in the GFZ, it was seen that systematic errors were observed, and serious distortions occurred in the signals (Figure 5). For this reason, the JPL data were also reanalyzed using the CSR DDK3 mean submodel. Thus, systematic errors were eliminated, and signal losses were corrected (Figure 6). Among the solutions obtained from the JPL data center, the DDK3 filter technique was deemed appropriate as in the other two data centers.

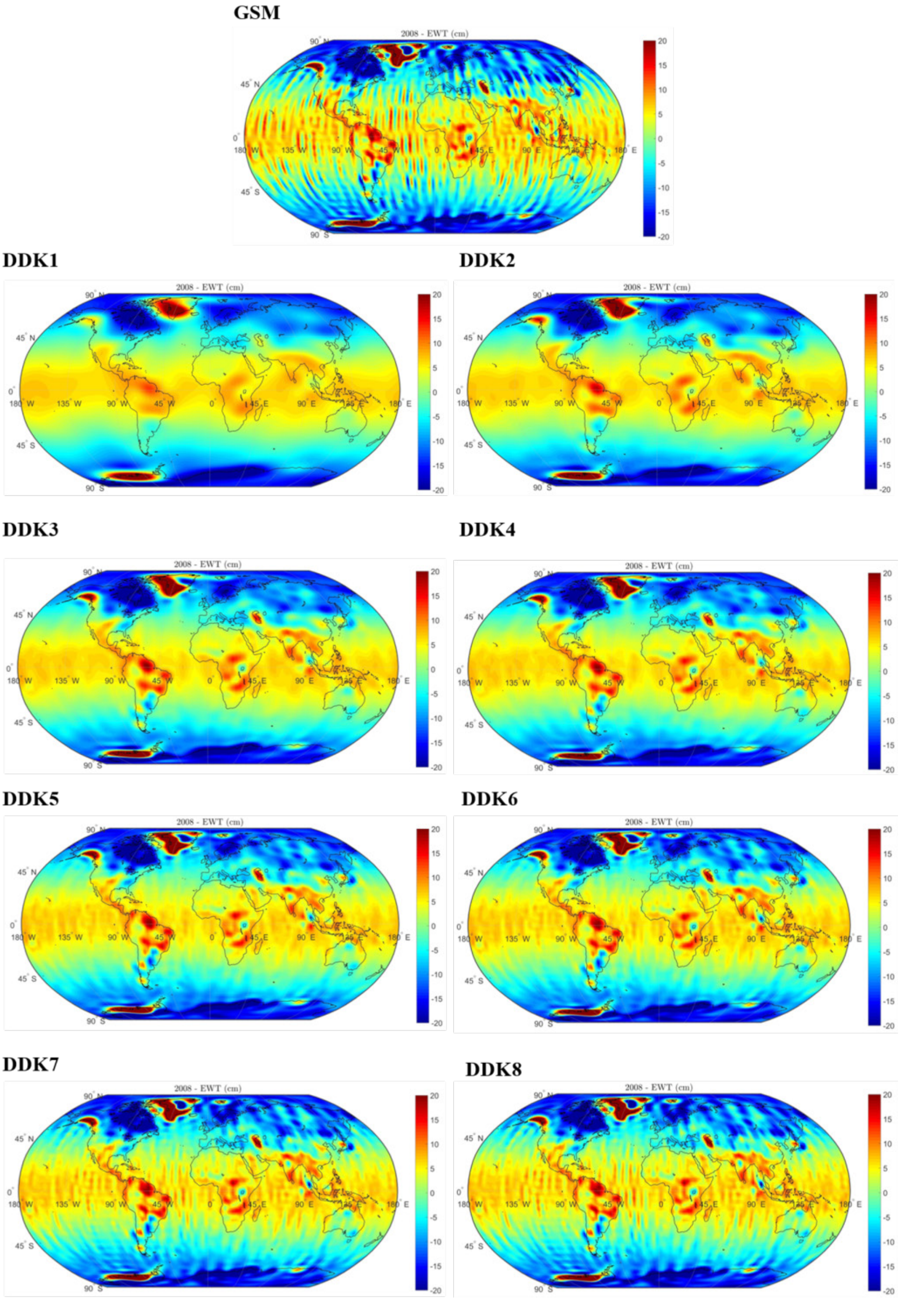

Figure 3. Comparison of DDK filters over EWT solutions of GRACE/GRACE-FO Level-2 Version-06 data created with the long-term average model from GFZ data

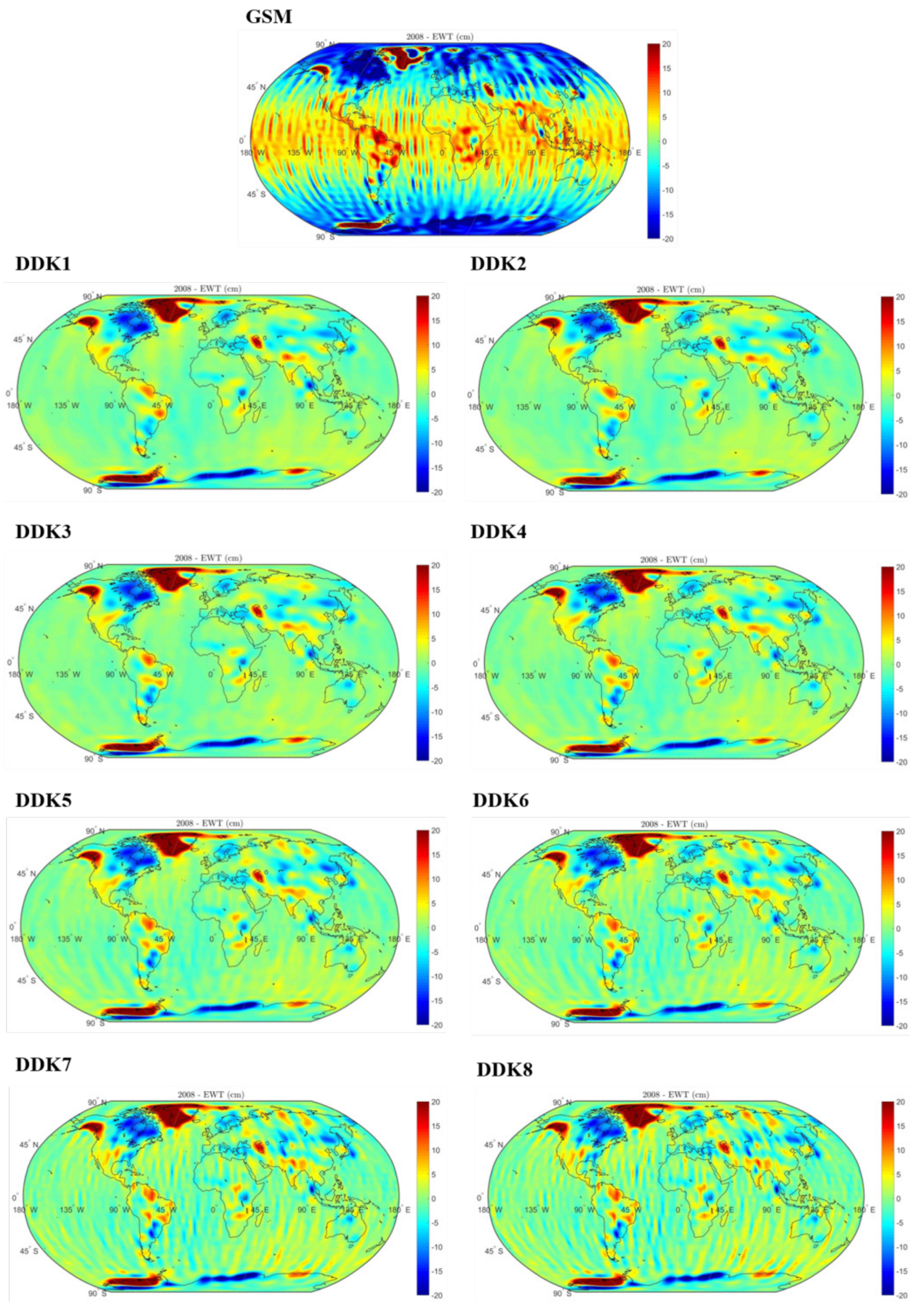

Figure 4. Comparison of DDK filters over EWT solutions of GFZ GRACE/ GRACE-FO Level-2 Version-06 data created with CSR DDK3 long-term average submodel

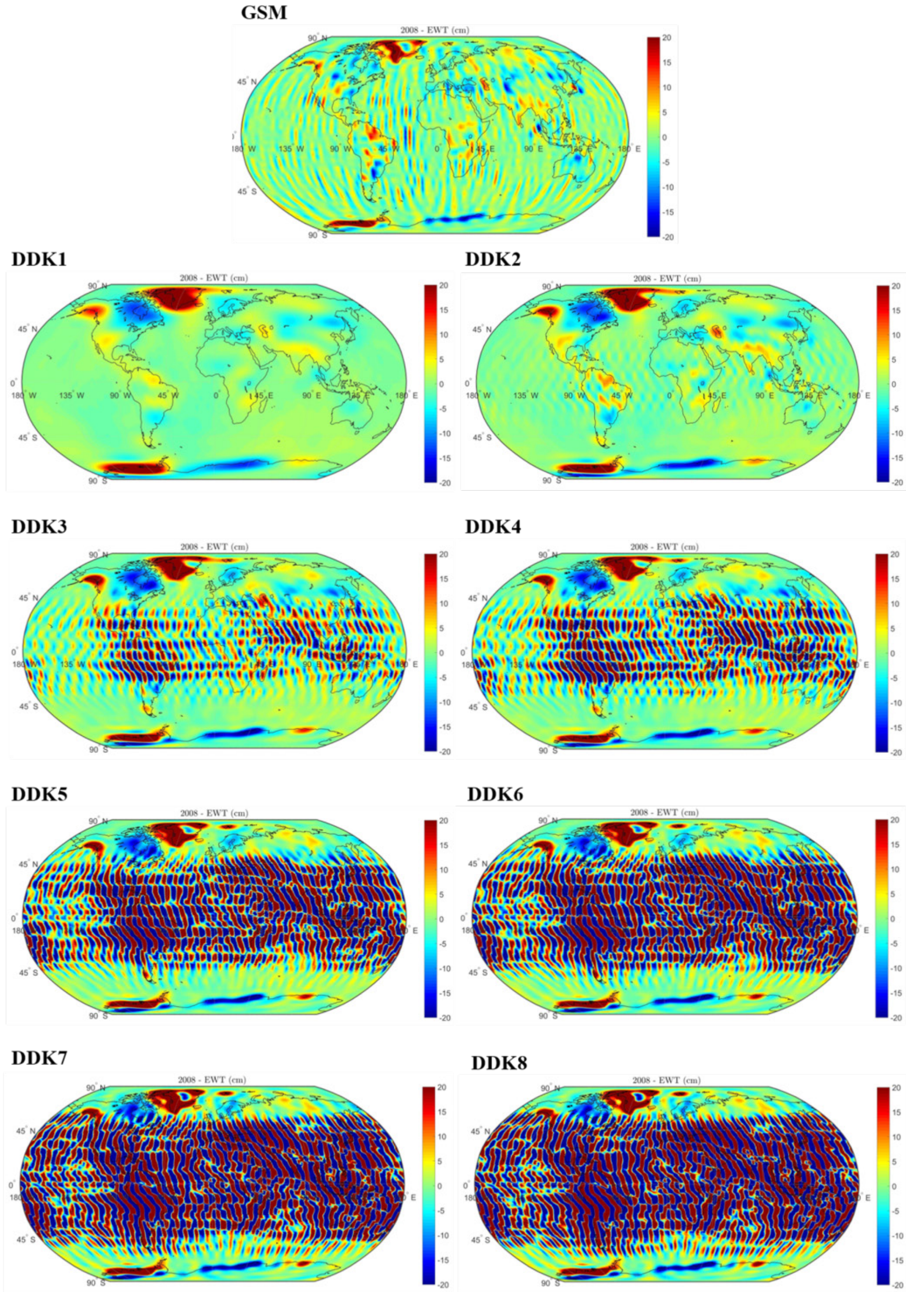

Figure 5. Comparison of DDK filters over EWT solutions of GRACE/ GRACE-FO Level-2 Version-06 data created with the long-term average model from JPL data

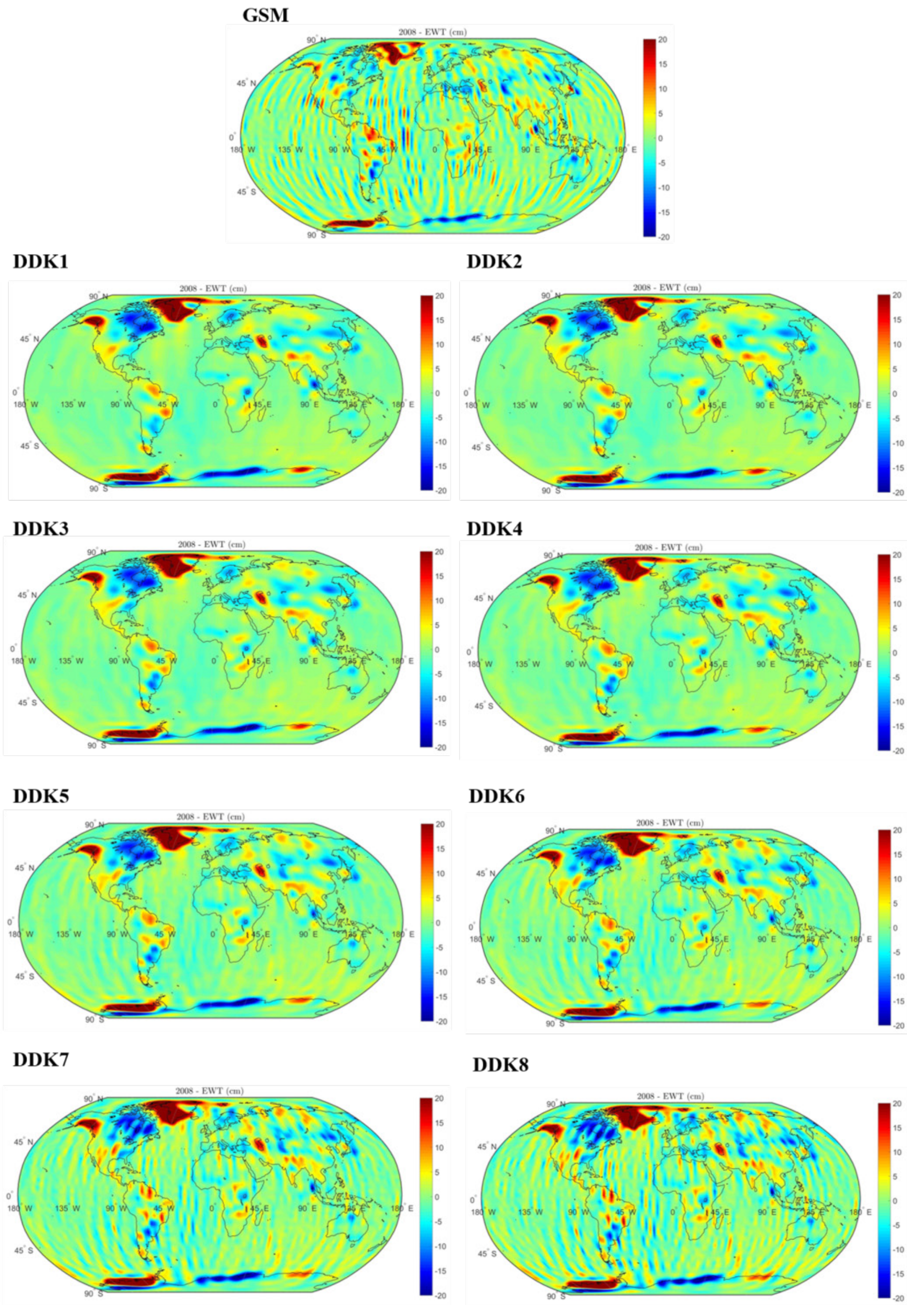

Figure 6. Comparison of DDK filters over EWT solutions of JPL GRACE/GRACE-FO Level-2 Version-06 data created with CSR DDK3 long-term average submodel

The DDK filtering technique was applied and evaluated on the EWT solutions of the three data centers selected above to obtain the GRACE/GRACE-FO Level-2 Version-06 data. In addition, Gaussian filtering techniques at different radius over GSM were applied to the solutions. Gaussian filters were also evaluated over the EWT solutions of 2008 in order to be compared with the solutions created with the DDK filters. Since the problems experienced when DDK filters were applied to the model created by averaging the solutions obtained from the previously mentioned GFZ and JPL data centers were also seen in the Gaussian filtering technique, the errors were eliminated by using the CSR DDK3 average model, which was chosen as the sub-model here, and then Gaussian filters were applied to the solutions. Looking at the relevant solutions, it is seen that the Gaussian filters applied at 240 and 340 km radius can eliminate the correlation effects by preserving the signals and resolution, but the signals become too soft and begin to affect the accuracy in the 530 km radius filtering. In other words, the resolution and signal accuracy decrease as the filter radius increases.

Considering the solutions of CSR, GFZ, and JPL data centers (Figure 7), the availability of filters applied in 240 km and 340 km radius is appropriate. Although the stripes in the north-south direction are somewhat evident in the Gaussian filter with a radius of 240 km, they do not change the accuracy much. As mentioned before, DDK1 approximately corresponds to the Gaussian filter with a radius of 530 km, DDK2 to the Gaussian filter with a radius of 340 km, and DDK3 to the Gaussian filter with a radius of 240 km.

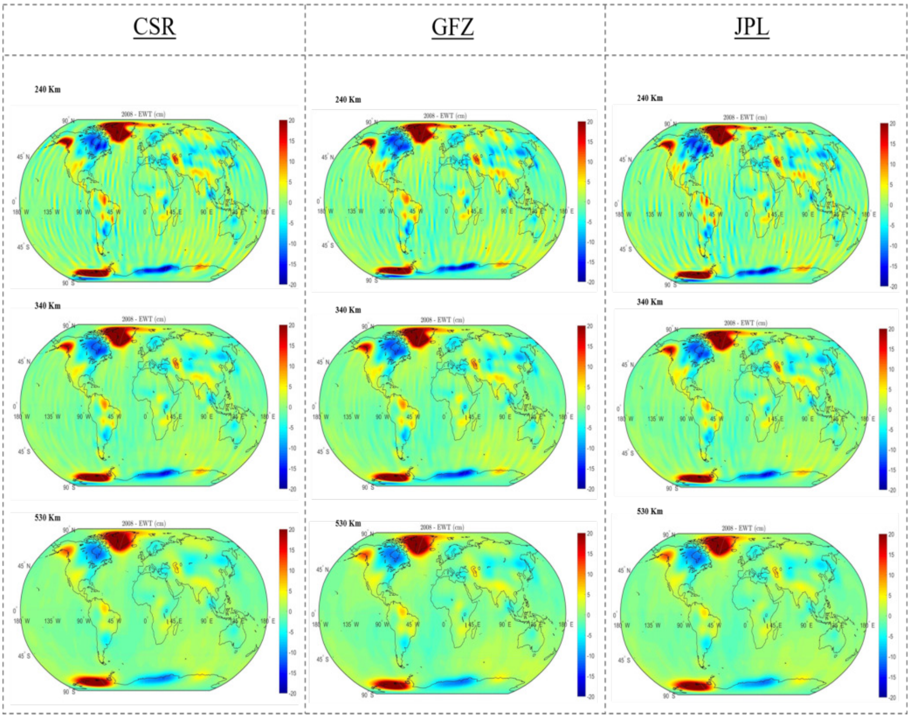

Figure 7. Comparison of CSR, GFZ, and JPL GRACE/GRACE-FO Level-2 Version-06 data on 240 km, 340 km, and 530 km radius Gaussian filters on EWT solutions

6. Results

The study compared the results of different data centers and different filtering techniques over the GRACE and GRACE-FO EWT data solutions. At the same time, the methods used to eliminate the errors and correlations of the data received from different data centers and which have various model-based errors, are mentioned. In line with the data obtained, a long-term average model was created on the EWT changes obtained from the GRACE and GRACE-FO Level-2 Version-06 data obtained from the CSR data center, and the model was compared within itself. In the results obtained, no model-based errors affecting the accuracy were encountered in the long-term average model created with the data of the CSR data center. Later, when DDK and Gaussian Filtering Techniques were used, it was observed that the correlation effects were also eliminated at various radius. However, in the EWT changes created as a result of the GRACE, GRACE-FO Level-2 Version-06 data obtained from the GFZ and JPL data centers, model-based errors were observed that affect the accuracy when each data center is inserted into the long-term average model within itself. In order to eliminate these errors, the average model consisting of the CSR DDK3 data set, which does not cause any model-based errors when inserted into the mean model and is thought to have sufficiently eliminated the correlation effect, was used. By subtracting the relevant average models from this average model used, model-based errors of the data received from GFZ and JPL data centers are also eliminated. When DDK and Gaussian filters are applied to the resulting models, ideal accuracies were achieved in some radius filters.

Within the scope of the study, Gaussian radius were chosen as 240, 340, and 530 km in order to compare the results of DDK and Gaussian filters with each other. It has been observed that the correlation effects are eliminated without affecting the accuracy of the data applied with Gaussian filters with radiuses of 240 and 340 km. However, while the filter at a radius of 530 km removed the correlation effect, it caused softening in the signals and affected the accuracy in some regions. When the DDK filters were examined, it was found that the Gaussian filter with a radius of 530 km and the DDK1 filter had a similar problem. It is also seen that the correlations in the north-south directions increase as you go from 1 to 8 in the DDK filters. DDK3 filter data provide ideal viewing.

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