

**INNOVATIVE MATERIALS IN ENGINEERING:
BIO-BASED APPROACHES AND
NANOSTRUCTURED ENHANCEMENTS**

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PREFACE

This book, "Innovative Materials in Engineering: Bio-based Approaches and Nanostructured Enhancements," is a comprehensive exploration of advancements in material engineering, focusing on sustainable and innovative solutions.

The first section examines the incorporation of hemp as a construction material within the building industry. This research emphasizes the importance of hemp's minimal carbon footprint, quick renewability, and biodegradable characteristics as the industry increasingly prioritizes sustainability to reduce environmental effects. It examines the historical backdrop of hemp use, highlighting its capacity to rejuvenate local economies and provide healthy living environments. This section tries to highlight the benefits of hemp over conventional materials in promoting a more sustainable building sector.

The second part looks at a binary mix of Congo red and bromocresol green dyes to find out how well the LDPE/CHNP bio composite works as an adsorbent to remove dyes from wastewater. The research shows that the integration of chitosan nanoparticles into a low-density polyethylene matrix improves the efficacy of the adsorbent. Multiple parameters, such as pH, contact duration, temperature, starting dye concentration, and adsorbent dose, are tuned to enhance sorption capacity. The results indicate that the LDPE/CHNP bio composite is a viable and sustainable option for environmental remediation, especially in wastewater treatment.

In the third section, global environmental challenges, including resource depletion and climate change, which provide significant threats to ecosystems and public health, were examined. This study aims to create sustainable composite materials in the Khyber Pakhtunkhwa (KPK) area of Pakistan via the utilization of recycled fibers and bio-based polymers. A mixed-methods approach, in conjunction with local businesses and stakeholders, demonstrates that these composites not only comply with industry requirements but also provide substantial environmental advantages, such as diminished carbon emissions and decreased energy use. The results underscore the need for regulatory assistance, capacity enhancement, and continuous research to facilitate the use of sustainable materials in the area.

The fourth section offers a detailed examination of the progress in nanostructured composites, particularly their roles in improving paint corrosion resistance. This investigation highlights the significance of nanotechnology in formulating novel corrosion protection measures and examines the synthesis techniques and performance mechanisms that enhance their efficacy. The study seeks to stimulate more research in enhancing these materials for wider uses across many sectors.

Chapter five examines occupational health and safety within the textile sector, with a specific emphasis on exposure to cotton dust. It examines the detrimental health impacts of cotton dust on workers, including respiratory conditions such as byssinosis. Furthermore, it offers insights on engineering controls, workplace practices, and regulatory measures

designed to mitigate dust-related hazards and promote a safer work environment.

The last section addresses pre-treatment methods in textile finishing, with a particular emphasis on cotton fibers. It analyzes the difficulties and advancements in bleaching methods, focusing on the optimization of hydrogen peroxide bleaching to reduce energy usage and environmental effects. This chapter examines the importance of pre-treatment in improving the quality and sustainability of textile goods.

This book aims to enhance the existing knowledge of sustainable materials and creative engineering techniques through the presentation of multidisciplinary studies. I express my sincere appreciation to the writers, researchers, and the UBAK publishing team for their significant contributions to this project. I hope this compilation proves to be a valuable resource for researchers, professionals, and students pursuing sustainable and innovative engineering solutions.

Assist. Prof. Dr. Grkem YUMUŐAK

TABLE OF CONTENTS

PREFACE..... v

TABLE OF CONTENTS.....ix

CHAPTER 1

**THE POTENTIAL AND APPLICATION EXAMPLES OF HEMP
USAGE AS A BUILDING MATERIAL.....(1-26)**

Assist. Prof. Dr. Özlem ÖZKAN ÖNÜR

Eda KAYA

CHAPTER 2

**EVALUATION OF DUST EXPOSURE IN THE COTTON
TEXTILE INDUSTRY.....(27-36)**

Lecturer Fatoş Ceren ŞAHİN

CHAPTER 3

**BASIC PRE-TREATMENT PROCESSES OF COTTON
TEXTILE PRODUCTS.....(37-54)**

Lecturer Fatoş Ceren ŞAHİN

CHAPTER 4

**BIOSORPTION OF DYE FROM SYNTHETIC WASTEWATER
USING CHITOSAN NANOPARTICLES AND LOW-DENSITY
POLYETHYLENE (CHNP/LDPE) BIOCOSMPOSITE AS
ADSORBENT.....(55-87)**

Oluwaseun Adelaja Adekoya

Ransome Olaoye Opeyemi

Olumide Adebisi Elijah

CHAPTER 5

**ENVIRONMENTAL IMPACTS OF BIO-BASED POLYMER
MATRICES AND RECYCLED FIBERS: A COMPREHENSIVE
ANALYSIS WITHIN KPK, PAKISTAN.....(88-112)**

Abdul Jalil

Taqwa Syed

Irfan Mateen

Abbas Ali

Mansoor Ali Khan

CHAPTER 6

**EFFECTIVENESS OF NANOSTRUCTURED COMPOSITES IN
ENHANCING PAINT CORROSION RESISTANCE
PROPERTIES.....(113-120)**

Debotosh Roy

Assist. Prof. Dr. Sandeepan SAHA

BÖLÜM 1

THE POTENTIAL AND APPLICATION EXAMPLES OF HEMP USAGE AS A BUILDING MATERIAL

Assist. Prof. Dr. Özlem ÖZKAN ÖNÜR
PhD Student Eda Kaya

INTRODUCTION

Today, the construction industry is progressing towards reducing environmental impacts by focusing on sustainability. Global environmental issues have led the construction sector to seek more environmentally friendly materials, taking into account factors such as carbon footprint and the life cycle of structures. This approach supports economic and social sustainability by providing energy efficiency with low maintenance costs [1]. Carbon footprint measures the greenhouse gases emitted during the process from the production to the use of building materials. Sustainable materials aim to minimize this footprint. These materials also offer sustainable solutions throughout the life cycle of structures with their long-lasting, durable, and recyclable properties.

Hemp is an annual, herbaceous, and dioecious flowering plant belonging to the Cannabinaceae family [2]. It is believed that hemp, with origins dating back to 850 BC, first emerged in Asia and India [3]. Hemp, which is divided into various subspecies under the Cannabis genus, is cultivated for fiber and drug production. Cannabis sativa is used for fiber production, while Cannabis indica is used for

pharmaceutical raw materials [4]. In recent years, hemp has become one of the plants that has attracted intense interest from the scientific community worldwide. In addition to its medical, food, and recreational uses, it has also been an important raw material in the textile industry for thousands of years [5].

Hemp, when used as a building material, offers significant advantages in terms of environmental, economic, and social sustainability. Its low carbon footprint, rapid renewability, and biodegradable properties support environmental sustainability, while its potential to revitalize local economies and provide energy efficiency contributes to economic sustainability. Additionally, hemp-based building materials serve social sustainability by creating healthy living spaces.

This study examines how hemp can be integrated into the construction industry from the perspective of innovation and environmental responsibility. It addresses the historical use of hemp and its rediscovery in the context of sustainable building materials today. By evaluating its advantages compared to traditional building materials, it aims to highlight the potential for creating a sustainable construction industry. In this way, significant steps can be taken towards a more sustainable construction sector by reducing the environmental impacts of future buildings. The study will first briefly touch on the historical uses of hemp, then focus on the importance of sustainable building materials and hemp's potential in this field. The aim is to examine the potential of hemp as a building material and its effects on environmental sustainability, and to raise awareness in this

area. In this context, by bringing together existing literature knowledge and practical examples, the potential of hemp as a sustainable alternative for the construction industry will be emphasized, and a guiding resource will be created for future research and applications.

HISTORICAL USES OF HEMP AND ITS REDISCOVERY

Clarke and Merlin's work "Cannabis: Evolution and Ethnobotany" comprehensively examines how cannabis has been used from ancient times to the present day [6]. Duwall's book "Cannabis" evaluates the historical place of cannabis within the framework of botanical science. Thompson's studies on Mesopotamian plants, especially his article "Assyrian Prescriptions For Treating Bruises or Swellings" shed light on the use of cannabis in ancient times [7]. From a medical history perspective, Bayat's book "History of Medicine" and Carod and Artal's article "Psychoactive Plants in Ancient Greece" provide important information about the medicinal use of cannabis [8]. Zuardi's article "History Of Cannabis As A Medicine: A Review" is an important source on the use of cannabis for meditation purposes in India [9]. "The Assyrian Dictionary of The Oriental Institute of The University of Chicago" has been used to examine the place of cannabis in Assyrian and Akkadian languages. Dölen's book "History of Textiles" provides important information about the presence of cannabis in Anatolia [10], while the Çatalhöyük excavation report documents the earliest times cannabis was seen in Anatolia [11]. Cahit Günbattı's work examining the Kültepe Tablets and Saba's article reveal the role of cannabis in textile trade between Mesopotamia and Anatolia [12]. This

study aims to bring a new perspective to the discussions on how cannabis was used by ancient societies and its presence in Mesopotamia and Anatolia. Additionally, the advantages obtained by ancient societies through the use of cannabis have also been examined.

The historical role of hemp in East Asia began in the Holocene Era (approximately 12,000 years ago), and it is believed that the homeland of hemp is Central Asia. Hemp, first used as a food source by hunter-gatherers, reached China around 9000 BC [13]. In China, hemp was used as food and medicine around 4000 BC, gaining particular importance for medicinal purposes (treatment of malaria, infertility, rheumatism) during the reign of Emperor Shen-Nung. In 3000 BC, hemp reached the Korean Peninsula and was used as a raw material for textile products [13]. In China, hemp began to be used as a psychoactive substance from the 16th century BC. Archaeological findings have revealed that fabric was produced from hemp during the Chou Dynasty period (13th century BC–3rd century BC). Hemp, which was also used in paper production in China (during the Western Han Dynasty, 206 BC–8 AD), stood out with its strong and waterproof structure. In maritime activities, ropes and sails made from hemp played an important role in China becoming a naval power [14].

There is no direct information about hemp or hemp products in early trade records such as the Kültepe tablets (1950-1750 BCE). This situation can be attributed to reasons such as hemp not yet being widespread in Mesopotamia and Anatolia, being referred to by different names, or having low commercial value [13]. Although the existence of words meaning rope such as "ishamina," "ishamanta," "ishimanas"

during the Hittite period suggests that hemp might have been used in rope making, there is no definitive evidence [10].

Although it is thought that hemp might be among the seeds found in excavations (8th century BC) in Gordion, the center of Phrygia, no definitive conclusion has been reached on this matter. The prevailing view is that hemp was brought to Anatolia, Europe, and the Mediterranean in the 5th century BC by the Scythians, a nomadic people of Central Asian origin. Hemp seeds and burning tools found in the Pazyryk Kurgan in the Altai Mountains (8th-7th centuries BC), along with Herodotus's accounts of the Scythians using hemp in their rituals, support this view [15].

It has been stated that hemp was introduced to the Western world through the Scythians. Strabo mentioned that shamans of a Thracian tribe performed rituals using a plant thought to be hemp. The Cilician physician Dioscorides named the hemp plant "kannabion" and emphasized its importance for medicine and textiles. Galen of Pergamon noted the pain-relieving properties of hemp and warned about the dangers of excessive consumption [16]. Hemp was used in medicine, psychoactivity, and textiles during the late ancient period. Records of the Greek tyrant Hieron II importing hemp from Spain indicate that this plant was used in ship technologies. However, the spread of hemp in the Mediterranean was late; Roman and Scandinavian sailors began using hemp in ship technology between the 1st and 10th centuries AD [6]. Materials made from hemp are more durable than other fibrous plants such as flax and papyrus. This feature increased the duration ships could stay at sea. For example, in 1492 AD,

Christopher Columbus's ships were equipped with hemp ropes; this played an important role in the successful realization of exploration voyages [14].Figure 1 shows the hemp plant.



Figure 1. The hemp plant [17]

Literature studies on hemp in Turkey comprehensively address the various uses and economic potential of hemp. Numerous studies have been conducted on the use of hemp in areas such as food, health, energy, textiles, and asphalt.[4] Examined the use of hemp in bakery products and its positive effects on health [2]. Revealed the therapeutic properties of hemp in the field of health [18]. Investigated the potential of hemp as an energy source addressed the environmental benefits of hemp and its use in textile production [19]. Examined the effect of hemp fibers in asphalt concrete mixtures and showed that these fibers improve mechanical properties [20]. Examined hemp production in the Ottoman and Republican periods from a historical perspective [21]. Investigated the effect of high temperatures on the germination of hemp seeds [22]. Finally, evaluated the economic feasibility of hemp in the Vezirköprü district of Samsun [23].

Hemp has a wide range of applications. While some varieties are considered as raw materials for drugs and pharmaceuticals, its fibers are recognized as one of the oldest weaving materials in human history. The seed, stalk, and flower of hemp are used in various ways. Hemp seeds can be processed into food or flour by cracking their shells. The oil obtained through pressing is used in food, bio-fuel, paint, and cosmetic products. Seed meal is utilized in animal feed, beer, or protein powder production. The stalk of hemp, after fiber separation, is used as a raw material in products such as fabric, textile products, panel production, cellulose, and paper. The remaining stalk after fiber separation is used as animal feed, compost, animal bedding, and as a mortar material in the construction industry. Hemp flower is generally used in the pharmaceutical and cosmetic industries, while its pulp is used as fish feed, fertilizer, and animal bedding [24].

Hemp was used in equipment such as ropes and cables for the navy during the Ottoman period [21]. The first major investment related to hemp in Turkey was the Taşköprü Hemp Factory established by Sümerbank in Kastamonu in 1946; however, the factory closed in 1951. The Hemp Industry Institute, established in 1945, aimed to produce twine and canvas from hemp fiber. However, due to jute imports from India and other factors, production gradually declined. By 2015, hemp production had decreased to 10 decares. As a result of the factory, which was privatized in 1998 and closed in 2004, purchasing cheaper hemp from abroad, production almost completely ceased [25],[26].

In recent years, hemp has been rediscovered and has gained significant value in the context of sustainable building materials. As an

environmentally friendly and renewable resource, hemp is used in various applications in the construction industry. Its fibers are preferred in the production of lightweight, durable, and highly insulating materials, while hemp concrete (hempcrete) stands out as a lightweight material that provides high thermal insulation and offers advantages in terms of carbon absorption. These building materials increase energy efficiency while minimizing environmental impacts by reducing carbon emissions. Additionally, hemp's rapid growth process and low water consumption make it an attractive ecological building material. These properties of hemp make it an ideal option for modern sustainable construction solutions and contribute significantly to supporting the ecological transformation in the construction sector.

HEMP AS A SUSTAINABLE BUILDING MATERIAL

Sustainable building materials are a critical area developed today to minimize environmental impacts and optimize resource use. In this context, hemp stands out as a notable material in sustainable construction practices. Thanks to its ecological advantages such as rapid growth process and low water requirements, hemp is considered an environmentally friendly alternative in the construction sector. Hemp holds an important place in the building industry as one of the sustainable and durable natural fibers. The hemp plant can grow up to 3 meters in as short as four months and can be harvested three times a year; this feature makes it a fast-growing and renewable material. It stands out as an eco-friendly option as it does not emit toxic gases during processing and has a low environmental impact [27].

One of the most common uses of hemp in the construction industry is insulation materials. It is particularly preferred in the production of insulation mats and insulation panels. These products increase the thermal comfort of interior spaces by providing energy efficiency and support energy savings. Figure 2 shows example views of hemp insulation material.



Figure 2. Hemp insulation material [28]

Wall blocks produced using hemp fibers and lime are used as infill material in the interior walls of buildings. These hemp-lime composites are an ideal solution for increasing durability and improving insulation properties, especially in timber-framed building systems. Such uses of hemp play a significant role in sustainable construction practices, offering structural and environmental advantages.

Hemp building material is produced by mixing the woody core of the hemp plant with lime and water. This mixture is shaped into blocks, cured, and then delivered to the construction site [29]. This environmentally friendly and sustainable alternative can be processed on-site or obtained as pre-manufactured blocks [30]. Figure 3 shows hemp building material.



Figure 3. Hemp building material [31]

Hemp stands out as a robust and durable building material due to its lightness and high strength. It reduces the carbon footprint by absorbing carbon from the atmosphere and is environmentally friendly as a highly efficient agricultural product. Its natural insulation properties maintain indoor temperature and provide energy savings. Additionally, hemp, which is generally fire-resistant, contributes to fire safety with its non-flammable properties. Its moisture-absorbing feature prevents decay and mold formation. Its moldability within forms and flexible design features allow it to adapt to different architectural styles [29],[30].

There are several important factors to consider in the use of hemp. Firstly, the mechanical performance of hemp is lower compared to traditional building materials such as concrete and steel. Therefore, this performance difference should be taken into account in the design and application of structures using hemp. For effective use of hemp, it is crucial to mix and apply the material in the correct proportions. Careful mixing and application directly affect the performance and durability of the material. Consequently, careful control and

management are essential in the construction and application processes of hemp [32].

POTENTIAL USE AND CURRENT STATUS OF HEMP-ENHANCED BUILDING MATERIALS IN TURKEY AND OTHER COUNTRIES

Hemp production in Turkey is experiencing a revival, but its use as a building material has not yet become widespread. Current legal regulations and incentives hold significant potential for increasing the use of hemp in the construction sector.

The hemp plant contributes to various market segments with its diverse products such as seeds, oil, and fiber, and is cultivated for commercial or research purposes in more than 47 countries worldwide. Since 2011, a global increase has been observed in hemp production and cultivation areas.

According to data from the United Nations Food and Agriculture Organization (FAO), hemp production statistics are available for 16 countries. Canada, China, Chile, France, and North Korea are prominent countries in hemp production.

The USA, on the other hand, is the largest importer of hemp products, sourcing most of its seeds and fibers from Canada and China. With the 2014 Farm Bill, the US government allowed research on industrial hemp production, leading to a rapid increase in hemp production and research in the USA.

The development of the US hemp industry has the potential to cause significant changes in global trade, potentially reducing US hemp imports. Figure 4 shows the countries where hemp is cultivated.



Figure 4. Countries where hemp is cultivated [33]

As consumer demand for organic and environmental sustainability increases, the growth potential of the global hemp market is also rising. In Turkey, hemp seed production is primarily carried out in Samsun [34]. Industrial hemp production was legalized in 19 provinces in 2019 [24]. Figure 5 shows the hemp cultivation areas in Turkey.



Şekil 5. Hemp cultivation areas in Turkey [24]

Hemp lime and hemp insulation materials are among the few potential application areas that stand out in the construction sector in Turkey.

Hemp lime (Hempcrete)

The use of hempcrete in Turkey has begun to be seen, especially in small-scale ecological house projects. This material is preferred as an environmentally friendly building material due to its high insulation properties and carbon neutrality. The application of hempcrete, used in some ecological village projects and individual house constructions, is shown in Figure 6.



Figure 6. Hemp lime [17]

Carmeuse has developed special lime products for designers, craftsmen, and homeowners to meet the needs in hemp construction. "Hempcrete" is a concrete-like natural building material created by binding hemp stalk with lime. The very lightweight hemp blocks reduce transportation energy while also lightening the load on the structure. According to analyses in the construction industry, this material can last up to 600 years. Hemp, made from natural materials and containing no chemicals, improves the quality of life by providing better ventilation in buildings. Most importantly, hemp, being a completely organic and renewable material, is both healthy and economical.

Hemp Insulation Materials

Insulation materials produced from hemp fibers are particularly preferred in environmentally friendly construction projects due to their high thermal and sound insulation properties. Although the use of these materials is not yet widespread in Turkey, they are among the potential areas of application. Bio-based economies are increasingly becoming a part of our daily lives. As the search for building and insulation materials with carbon-negative footprints continues, hemp construction stands out as a natural and sustainable solution. Thanks to their moisture regulation capabilities, hemp building materials have become a preferred bio-product both for their use in insulation and for providing a healthy indoor climate. Examples of thermal insulation materials obtained from industrial hemp are given in Figure 7.



Figure 7. Examples of thermal insulation materials derived from industrial hemp

France is one of the world's leading countries in hemp production and utilization. Hempcrete is widely used in this country, especially preferred in the construction of ecological houses. Due to its

lightweight, breathable, and energy-saving properties, hempcrete is a popular building material in France. Industrial hemp can be mixed with plaster and binding agents to produce lightweight panels that can compete with drywall. Additionally, hemp and lime mixtures create high-quality plasters. Hemp stalks, rich in silica, transform into a stone-like material when mixed with lime. The most advanced technology in this field is found in France. The renovation of walls from a 16th-century historical building using industrial hemp is shown in Figure 8, while the view of a structure built with industrial hemp building material in France is given in Figure 9.



Figure 8. Restoration of 16th century historical building walls with industrial hemp



Figure 9. View of the building constructed with industrial hemp building material located in France [36]

In the history of architecture and construction, it is known that hemp was used as mortar in the "bridge piers" of the Merovingian bridges in France, as shown in Figure 10.



Figure 10. Merovingian bridge

Hemp production and use in the USA gained momentum with the 2014 Farm Bill. Hemp-based building materials are particularly preferred in environmentally friendly architectural projects. The number of houses built using hempcrete is steadily increasing in states such as Colorado and California. The USA is also making significant progress in the production and use of hemp-based composite materials.

Canada is a significant hub for hemp production and processing. Hemp-based building materials are preferred in the country, especially in sustainable construction projects. In fact, some structures have been built entirely with hemp-based materials. Hemp insulation materials are also widely used in Canada.

The Canadian Hemp Trade Alliance (CHTA) is a national organization that supports Canadian hemp and hemp products worldwide. Established in 2003, this alliance aims to represent various stakeholders in Canada's hemp industry. Its members include farmers,

processors, manufacturers, researchers, entrepreneurs, and marketers. Canada is currently the largest producer and exporter of hemp seed products such as hemp seeds, hemp oil, and hemp protein powder. Canada supplies 60-90% of the U.S. hemp import market. Canadian hemp seeds are generally of high quality because only hemp varieties listed in Health Canada's List of Approved Cultivars are permitted for use. Additionally, all hemp seeds from Canada are free from genetically modified organisms (GMOs).

RESULT

The hemp plant has significant potential among sustainable building materials due to its environmentally friendly properties and high performance. This plant, which stands out with its rapid growth process and high productivity, can yield crops several times a year. Its natural renewability also enables hemp to emerge as a sustainable building material.

Sustainable building materials are materials that consume minimal energy throughout their life cycles [37] These materials, designed in accordance with environmentally friendly and energy efficiency standards, offer many advantages in terms of both ecological and economic sustainability. In today's construction industry, sustainable building materials are of great importance in order to use resources more efficiently by minimizing environmental impacts. Hemp, which stands out with its energy efficiency, durability, and recycling properties, is a noteworthy alternative material in this context.

It is extremely important to consider the application areas and requirements of the material while improving the properties of construction materials. Materials are comprehensively characterized using various analytical techniques. In this process, the microstructure, morphology, chemical composition, and energy distributions of the materials are investigated [38].

Composite materials produced from hemp fibers overcome the shortcomings of newly obtained materials [39], [40-41]. The use of hemp as a building material offers advantages such as energy savings and long-term use while minimizing environmental impacts. This material stands out with its low energy consumption, high insulation capacity, and carbon-negative properties. Insulation mats, insulation panels, wall blocks, and other composite building components made from hemp fibers make significant contributions to sustainable building solutions. The use of these materials not only ensures energy efficiency but also plays an important role in achieving sustainable construction goals by increasing environmental sustainability. The adoption of hemp material can contribute to ensuring a greener and more durable future in the construction industry. The construction sector is producing more environmentally friendly and efficient construction solutions by adopting the use of sustainable materials such as hemp. Hemp's high insulation properties provide low environmental impact in construction processes. Additionally, the absence of toxic gas formation during processing and its low environmental impact support the preference for this material.

Findings in the literature indicate that hemp is an innovative and sustainable alternative with extensive potential for use in the construction industry. However, more research and standardization work is needed for large-scale applications. The potential offered by hemp is of great importance in terms of meeting the needs of future generations while preserving environmental balance.

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CHAPTER 2

EVALUATION OF DUST EXPOSURE IN THE COTTON TEXTILE INDUSTRY

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INTRODUCTION

The textile industry is known as a sector with a wide range of production that falls under the supply chain of the ready-made clothing industry. Natural fibers such as cotton and wool and synthetic fibers are used in the textile industry. This sector is related to the animal husbandry and agriculture sector due to natural fibers. It is also closely related to the petrochemical industry due to the use of synthetic fibers.

The cotton weaving industry is known as one of the most important segments of the textile industry. This sector is considered to be in the "dangerous" class according to the Workplace Hazard Classes Regulation (WHO, 1999).

In the cotton weaving industry, cotton is processed into yarn and the final product of the yarn, fabric. During this process, employees in this sector are exposed to chemical and physical factors. The most effective factor among these factors is known as cotton dust. Cotton powder is stated as an organic powder type. This type of organic dust can initially cause occupational lung disease in workers. This disease

is known as "bysinosis". However, if this stage progresses, permanent respiratory failure may occur (WHO, 1999).

According to the International Standards Organization, dust is defined as solid particles smaller than 75 microns that remain suspended in the air but collapse under their own weight. The size of dust particles generally varies between 1 and 100 micron meters in diameter. These particles settle slowly with the force of gravity. Dust types are listed below according to the working environment (WHO, 1999);

- Mineral Dusts: Crystal silica, quartz, coal, cement dusts
- Metal Dusts: Lead, cadmium, nickel, beryllium dusts
- Other Chemical Dusts: Not bagged chemicals and pesticides
- Organic and Herbal Dusts: Cotton, flour, wood, tea dusts, etc.
- Biological Dusts: Living particles, mold, spore, etc.

Dust particles are classified according to their physical, chemical and biological effects. The classification of dust particles is given below (Yasun, 2008; Tatar, 2014; Jones, 2015):

- Biological Dusts: Fibrogenic, toxic, carcinogenic, radioactive, allergic, inert dusts.
- Physically Dusts: Crystal, amorphous dusts.
- Chemical Dusts: Inorganic, organic dusts.

Cotton dust is produced as a result of the transportation and processing of cotton. It is stated that during the processing of cotton, it is cotton dust, not cotton fibers, that affects the health of employees.

Therefore, in the evaluation of cotton dust exposure, dusts that are free of fibers and have a particle size of less than 15 microns are taken into consideration (OHS, 2007).



Şekil 1. Exposure to cotton dust

The health effects of dust particles may vary depending on their type, such as silica, coal, asbestos, lead, wood and cotton. Information on the health effects and target organs of different dust particles is included in the table below (WHO, 1999).

Table 1. Health effects of dust particles (WHO, 1999)

Type of Dust	Health Effect	Target Organ
Silica	Silicosis	Lung
Coal Dust	Pneumoconiosis	Lung
Asbestos	Asbestosis, Lung Cancer, Mesothelioma	Lung
Lead Dust	Systemic Poisoning (blood and central nervous system)	from the Respiratory Tract to the Bloodstream
Wood Dust	Nose Cancer	Nasal Airway
Cotton Dust	Byssinosis	Lung

Conditions such as respiratory dysfunction and chest tightness are observed in workers exposed to cotton dust. These reactions can be defined as byssinosis. However, because of extensive studies, some disorders other than these reactions have emerged. For this reason, in 1986, science candidates gathered in Manchester to discuss cotton dust exposure. These scientists described a number of reactions and identified research goals. These targets are called the "Manchester criteria". These are the reactions identified within the Manchester criteria: feeling of tightness in the chest, hyperactivity in the respiratory tract, chronic bronchitis, workplace fever, and decreased respiratory function (Bakırcı, 1996).

Byssinosis occupational disease; It is known as a lung disease that occurs when exposed to organic dust during the processing of plants such as cotton, hemp and flax. This disease is evaluated in two different ways: acute and chronic. Acute byssinosis is seen in people newly exposed to cotton dust. Symptoms of this disease include

cough, shortness of breath, wheezing, and acute changes in lung functions. Chronic byssinosis is found in people who have been exposed to cotton dust for 20-25 years (Bakırcı and Tümerdem, 2002).

When dust measurement values exceed acceptable exposure values, engineering solutions must be put forward. Dust equipment should be placed in machines to prevent the spread of dust particles into the environment in workplaces. At the same time, filtering the air in the work environment is another solution. It should be checked that the fans and filters of mechanical ventilation systems are working properly (OHS, 2007).

Masks should be selected based on the worker's exposure. Employees should be trained on the use and limitations of the mask. Masks should be properly cleaned, stored and controlled.

Workers should be informed about processes that may result in cotton dust exposure. The use of compressed air for cleaning devices and surfaces should be prohibited. If compressed air is used, the employee doing the cleaning must wear a mask and all other personnel who are not cleaning must leave the area. Cleaning clothes with compressed air should be prohibited. Waste must be discharged mechanically. Engineering control equipment and ventilation systems should be checked, cleaned and repaired (OHS, 2007).

Some preparations must be made for the transportation and cleaning of materials in different environments containing cotton dust. Cotton, cotton waste, and materials containing cotton dust should be

stacked, sorted, baled, discarded, or handled by other methods that reduce dust exposure to an acceptable level. In cases where a broom is used for floor cleaning, the broom should be used carefully to prevent dust from spreading into the air. During the collection of waste collected with long-handled brooms, precautions should be taken to ensure that the amount of dust released into the air is as low as possible. When cleaning machines with a brush or cloth, waste should be collected from top to bottom, as far away from the face as possible. Air should not be blown onto the machine surface during cleaning (OHS, 2007).

According to the dust control regulation, cotton dust respirable limit values are given in Table 2. The processes in which cotton dust is found are ginning, milling, spinning, weaving and confection. The cotton dust exposure limit value in ginning, cardboard and spinning mills is stated as 0.5 mg/m³. While this value is 0.75 mg/m³ in weaving enterprises, this value is expressed as 1 mg/m³ in confection enterprises (ÇSGB, 2024).

Table 2. Dust control regulation respirable cotton dust limit values (ÇSGB, 2024)

Cotton Dust Exposure Processes	Respirable Cotton Dust Limit Values (mg/m ³)
Ginning, Milling, Spinning	0,5
Weaving	0,75
Confection	1,0

International organizations have also specified specific values for cotton dust respirable exposure limit values. According to OSHA; it is expressed as 0.2 mg/m³ for yarn production, 0.75 mg/m³ for weaving and 0.5 mg/m³ for the cotton washing process. According to NIOSH and ACGIH, it is stated as 0.2 mg/m³ for all processes (OSHA, 2024).

Table 3. According to international organizations respirable cotton dust limit values (OSHA, 2024)

Organization	Processes	Respirable Cotton Dust Limit Values (mg/m ³)
OSHA	Yarn Production	0,2
	Weaving	0,75
	Cotton Washing Process	0,5
NIOSH	All Processes	0,2
ACGIH	All Processes	0,2

RESULTS

The textile sector has an important place in Turkey. The number of individuals working in this sector is also high. For the health and safety of working individuals, it is necessary to carefully comply with the legislation regarding occupational health and safety. Byssinosis disease appears to be common in textile workers exposed to cotton dust. The health of employees must be protected by taking into account the values of respirable cotton dust detected in some departments such as weaving, garments, etc. in textile industry.

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CHAPTER 3

BASIC PRE-TREATMENT PROCESSES OF COTTON TEXTILE PRODUCTS

Lecturer Fatoş Ceren ŞAHİN

INTRODUCTION

Finishing processes cover all the processes that the raw textile material undergoes until it becomes the final textile product and is offered for sale. Textile finishing; It consists of pre-treatment, coloring and finishing stages. Pre-treatment processes play the biggest role in textile finishing. Textile pre-treatment forms the basis of making the textile material ready for use. It is also stated as a preliminary preparation for other finishing processes. This process beautifies the appearance of the textile product. Foreign substances in the textile product are removed through pre-treatment processes.

Defects seen in the textile product as a result of textile finishing; 11% from finishing operations, 23% from dyeing and printing, 21% due to poor material quality, 24% due to biological, chemical and mechanical errors, 21% of it is due to pre-treatment errors. As a result of the initial finishing process of all white, dyed or printed fabrics, some irregularities in the fabric disappear. Improper pre-treatment and many of the errors that may arise are difficult to detect during the pre-treatment process.

Not all textile products need to undergo all pre-treatment processes. In some cases, only a simple washing process may be sufficient as pre-treatment. A good finisher can determine which finishing processes will be done, in which order, on which machines and according to which method, depending on the condition and type of the product. In this case, there are no definitive rules and decisions are made based on experience.

Application of textile materials to textile products can be done according to various methods. Extraction, impregnation, transfer, coating and spraying processes are among these methods. Extraction and impregnation processes have an extremely important place in textile finishing. However, increasing costs in the textile industry have increased competitiveness and the tendency towards lower-cost processes has increased. The textile industry constitutes the largest expense item in terms of energy costs.

Textile materials consisting of cotton fiber, which is the most common in nature, not only damages the fibers when processed at high temperatures, but also increases the costs of textile businesses. For this reason, the textile industry has tended to develop strategies to minimize the costs of the processes that need to be applied during production and to prevent environmental pollution by using environmentally friendly products. Cotton fibers have a very important place in the textile industry. It is known that cotton fibers have high water absorbency and good dry/wet strength. Today, it is

used in many areas of the textile industry, from underwear to outerwear and sewing threads (Polat, 2013).

Cotton fibers contain color pigments that prevent the natural white appearance of the fiber. Unless the fibers are dyed dark or black, it is necessary to bleach these natural color pigments (Lim, and etc 2004). In the bleaching process, fabrics with homogeneous, good hydrophilicity and desired whiteness are obtained by oxidation of natural color pigments and foreign substances in the fiber (Gürsoy, vd 2004). The global textile industry relies on sodium chlorite, hypochlorite and hydrogen peroxide systems (Shao, vd 2010). Although it is possible to achieve excellent whiteness and wetting properties with chlorine-based bleaching processes, it is replaced by hydrogen peroxide bleaching process due to environmental pressures (Gürsoy, vd 2004; Shao, vd 2010). Classical hydrogen peroxide bleaching provides satisfactory whiteness and is environmentally friendly. However, it also has disadvantages such as high energy requirement and damage to the fiber due to heavy bleaching conditions at high temperatures (Gürsoy, vd 2004; Lee, vd 2005). For this reason, research is being carried out to improve the process of bleaching cotton fibers with hydrogen peroxide.

Structure of Cotton

Cotton is known as almost pure cellulose. The non-cellulosic part consists of approximately 9.5% of components such as hemicellulose, protein, fat, minerals and wax (İbrahim, 2010). The

content of raw cotton fiber varies depending on the type of cotton, its origin, fiber maturity, weather conditions and agricultural conditions (Hebeish, 2009). The composition of typical cotton is shown in Table 1 (Lewin, 2006).

Table 1. The composition of typical cotton (Lewin, 2006)

Mature Cotton Composition (% Dry Weight)			Immature Cotton
Component	Typical (%)	Interval (%)	Typical
Cellulose	95	88 – 96	Decreases
Pectin	0,9	0,7 - 1,2	-
Protein	1,3	1,1 – 1,9	Increases
Ash	1,2	0,7 – 1,6	-
Wax	0,6	0,4 – 1,0	Increases
Total Hydrates	0,3	0,1 – 1,0	-
Organic Acids	0,8	0,5 – 1,0	Increases
Pigment	Small Amount	-	Increases
The Others	1,4	-	Increases

The degree of polymerization of cotton is between 9000 and 15000. Cellulose macromolecules are located in a certain order within the cotton fiber. About 420 macromolecules come together to form elementary fibrils, elementary fibrils come together to form microfibrils, and microfibrils come together to form macrofibrils. In this way, properly placed fiber elements form the crystalline region (Dayioğlu, vd 2007). The total of crystalline regions constitutes 65-70% of the entire fiber.

The remaining 30-35% of the fiber consists of the part described as "amorphous" or "easily penetrable regions" (Çoban, 1999).

Cellulose is a polysaccharide with the general formula $(C_6H_{10}O_5)_x$. Cellulose consists of repeating D-glucose units. Glucose units are 6-membered rings and are called pyranoses.

Cellulose polymer is formed as a result of a large number of P-D-Glycopyranose bonded via oxygen bridges over the 1st and 4th carbon atoms. Figure 1 shows the numbering of carbon atoms in the ring (Xu, 2009; Mather ve Wardman, 2011).

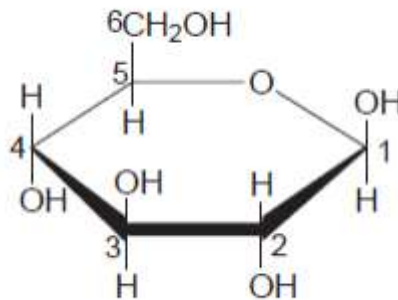


Figure 1. β -D- Glycopyranose (Polat, 2013)

The repeating unit in cellulose is cellulobiose, which consists of two glucopyranose units. The chemical formula of cellulobiose is shown in Figure 2.

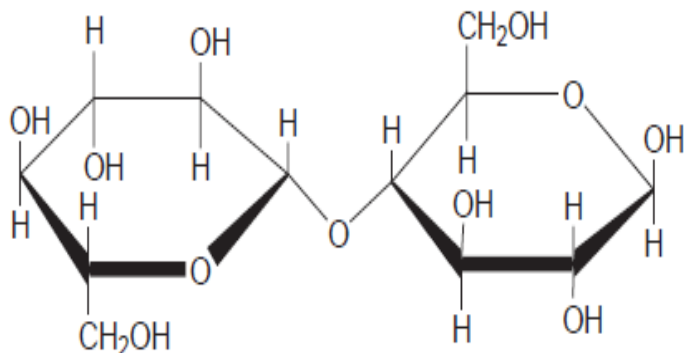


Figure 2. Cellulobiose (Polat, 2013)

The chemical structure of cellulose is shown in Figure 3. Pectin is present in the cell wall of cellulose as water-insoluble salts of calcium, magnesium and iron. Fats are generally known as products resulting from the esterification of glycerin with fatty acids.

Waxes are substances formed as a result of the esterification of fatty acids with long-chain monohydric alcohols. Ash varies depending on the composition of the cotton fiber.

The components obtained by burning various cotton samples are as follows; It is stated as 45% potassium carbonate, 11% potassium phosphate, 10% potassium chloride, 9% potassium sulfate, 9% calcium phosphate, 8% magnesium phosphate, 3% iron oxide and 1% other substances (Aniş, 1998).

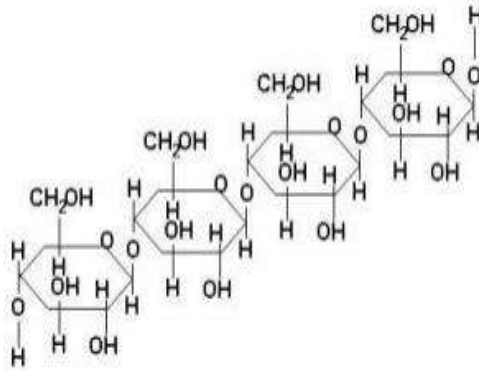


Figure 3. Chemical structure of cellulose

The outermost layer of the cotton fiber is the cuticle layer and is covered with wax and pectin. This layer covers the primary wall consisting of cellulose, pectin, wax and protein substances. The primary wall of cotton contains less than 30% cellulose, non-cellulosic polymers, neutral hydrates, uronic acid and various proteins.

The cellulose in the primary wall has a low molecular weight and its degree of polymerization (DP) is between 2000-6000. The inner part is referred to as the secondary wall. The secondary wall of cotton is almost 100% cellulose. The degree of polymerization is approximately 14000 and the molecular weight distribution is more uniform (Gordon and Hsieh, 2007). In the middle part, there is a channel called lumen. The layers in cotton fiber are shown in Figure 4 (Polat, 2013).

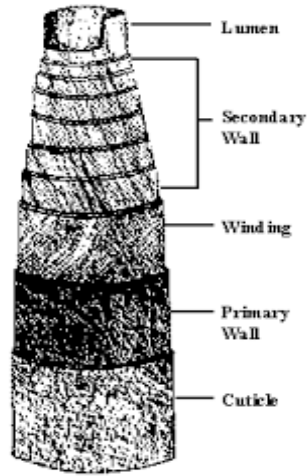


Figure 4. The layers in cotton fiber

Defects occur in cotton cells due to changes in climate and agricultural conditions, and as a result of the death of the cell before it can fully develop, fibers called "dead cotton" are formed. In dead cotton fiber, unlike normal cotton, the lumen is not completely dried, the cuticle layer is extremely thin and the secondary membrane is not completed (Dayioğlu and Karakaş, 2007).

There are definitely immature cotton cells inside the cotton cocoon. The ripening amount is important and affects the quality of cotton. Generally, 75% of commercial cotton is mature. In rare cases, a product that is over 90% ripe can be obtained. The average maturity rate is generally between 68-75%. Cotton with a maturity below this rate is considered dead cotton. Dead cotton breaks easily during yarn production and causes excessive losses. In addition, it is not preferred because it causes problems in dyeing (Dayioğlu and Karakaş, 2007).

Cotton fiber has a unique shine and its color is usually off-white. If it is collected late, this color becomes gray. The color of cotton varies depending on factors such as climate and environment (Dayiođlu and Karakaş, 2007; Gürsoy and Hauser, 2010).

Cotton fiber is a medium-strength fiber and ranks between wool and silk in terms of fiber strength. The tensile strength increases slightly when wet. The reason for the increase here is attributed to the decrease in the internal tension within the fiber under the influence of water.

Cotton, the core fiber, likes the humid, warm climate best. While China, America and India are the leading countries where cotton fiber is produced, these countries are followed by Pakistan, Brazil, Turkey, Uzbekistan, Egypt, Mexico, Iran and Sudan.

The quality of cotton fiber is greatly affected by the conditions in which it grows. The quality of the fiber is determined by its fineness and length. The best quality fibers are grown in Egypt and Sea Island, and the fiber length varies between 25-65 mm. Fibers of this quality are difficult to grow and are known as the most expensive fibers. Cottons with a fiber length of 13-33 mm are defined as standard cottons. American upland cotton is included in this group. This species is grown abundantly in Alabama, Georgia, the Carolinas and Virginia. Cottons with a length between 10-25 mm are low quality cottons and are grown in Asian countries (Dayiođlu and Karakaş, 2007; Mather and Wardman, 2011).

The density of cotton fibers is stated as 1.54 g/cm³, the moisture absorption value is 8.5%, the elongation at break is 6-8% in the dry state and 7-10% in the wet state. At the same time, the tenacity value of these fibers is 25-40 cN/tex and the thermal conductivity value is at a medium level.

Chemical Properties of Cotton Fiber

Acids act on the cellulose of cotton by hydrolyzing its glycosidic bonds. With the effect of hydrolysis, the long polymer chains of cellulose break and therefore the average degree of polymerization decreases. Cellulose fibers that are broken down by acids in this way are called hydrocellulose. The more fragmentation in hydrocelluloses, the more reducing properties they have, as the number of aldehyde-containing end groups increases (Dayıođlu and Karakaş, 2007; Mather and Wardman, 2011; Tarakçıođlu, 1979).

Cotton is resistant to alkalis. However, alkalis affect cotton in an oxygenated environment. While it is possible to boil cotton with 2% NaOH in an airless environment, in case of air flow, the structure of the cotton breaks down. Medium strength alkalis do not affect cotton in an airless environment. In the presence of oxygen, the fiber breaks down after the formation of oxycellulose (Dayıođlu and Karakaş, 2007).

The effect of oxidizing agents used to bleach cotton fibers on the fiber varies depending on the type, concentration, temperature and processing time of these oxidizing agents used. Treatment with

hypochlorite and hydrogen peroxide, sunlight and air can cause oxycellulose formation in cotton. When cotton is treated with oxygenated water, oxycellulose is formed if there are heavy metals such as iron (Fe), copper (Cu) and Manganese (Mn) in the environment (Dayıođlu and Karakaş, 2007).

Microorganisms such as mold bacteria and some types of fungi damage cotton. Since such microorganisms like moist and warm environments, the storage and processing environments of cotton are important in this respect. It is necessary to protect cotton from mold and microorganisms with appropriate methods (Dayıođlu and Karakaş, 2007).

In an oxygen-free environment, light does not have a damaging effect on cotton. However, when left under sunlight in an oxygenated environment for a long time, the oxycellulose rate increases and the fiber deteriorates. The presence of moisture and trace amounts of copper and other metals in the environment greatly accelerates the damage of cotton (Dayıođlu and Karakaş, 2007).

Pre-Treatment of Cotton Fabrics

All foreign substances on the cotton fiber must be removed by pre-treatment processes. Otherwise, it reduces the quality and efficiency of the finishing of the cotton material and even makes the finishing processes after the pre-treatment impossible.

As a result of an efficient pre-treatment process, it is not enough to remove foreign substances such as size, waste, oil, wax, pectin, hemicellulose, colored matter in or on the fibers that make up the textile product, and thus provide a good degree of hydrophilicity and whiteness. At the same time, thanks to a good pre-treatment process, costs resulting from correcting faulty dyeing and losses resulting from using second quality cotton are reduced.

Table 2. Basic pre-treatment process steps of cotton product (Aniş, 1998)

Processes	Aim of Processes	Type
Incineration	Smoothing the textile surface	Incineration
Desizing	Crushing and removing size, Swelling of cellulose	Extraction and Blowing
Hydrophilization	Removal of hydrophobic substances in textile fiber, softening of vegetable wastes, swelling of cellulose	Extraction and Blowing
Bleaching	Degradation of colored pigments, removal of vegetable residues	Oxidation and Extraction
Mercerization	Expanding the internal surface area, making the cross-section circular	Blowing

Pre-treatment process is carried out in order to prepare the textile product for other finishing processes and to improve the appearance of the product. Pretreatment of cotton fabrics consists of burning, desizing, hydrophilization, bleaching and mercerization processes. The type of finishing processes to be applied depends on

the quality of the product and the facilities of the business, and there is no obligation to perform these processes in a certain order or all of them (Çağiltay, 2012).

Fluff Burning

With the burning process, the fluff on the surface of the textile material is removed and the surface becomes smoother. The reason why burning is done as the first process in the pre-treatment department is that the product turns slightly yellow after burning. However, some sizes are cooked during burning, so burning can also be applied after desizing.

There is a fine pile on the woven cotton fabric. In many fabrics, especially cotton fabrics, it is desired that the fabric have a smooth surface. For this purpose, the fluff on the fabric is burned with burning machines without causing any damage to the fabric. (Erden, 2009). The surface properties and end-use properties of the fabric are improved by the firing process. Since the hairs on the fabric prevent the clarity of the print, the patterns become clear by burning these hairs in the burning process (Polat, 2013).

Desizing

Warp threads are sized in order to make the fabrics work more efficiently while weaving on weaving looms. With the sizing process, the warp threads are coated with natural and artificial sizing agents in the form of a thin film layer, which increases the performance in

weaving by ensuring that the fibers that are exposed to mechanical stress adhere better to each other, become more closed and stronger, and increase their lubricity.

Sizing agents are defined as natural or artificial substances that are macromolecular, capable of forming films and having a certain ability to adhere to fibers. Sizing aids, on the other hand, have smaller molecules, and their chemical structures and the effects they provide may differ among themselves. Softener, lubricant, wetter, dissolution enhancer, static electricity reducer, etc. items can be counted among these.

Boiling

Foreign substances contained in cotton fibers; It prevents cotton from getting regular liquor and getting wet during finishing processes (Yurdakul and Atav, 2004). The purpose of the boiling process is to remove these foreign substances (Shore, 1995). With the boiling process, the non-cellulosic substances contained in the cotton fiber are removed, giving the fiber a hydrophilic character. The boiling process generally takes place in sodium hydroxide solutions (1-4%) for 30-60 minutes. Many boiling processes are carried out under atmospheric pressure at 75-100°C. The boiling process can be carried out in a shorter time and using less alkali with pressurized machines that can operate at 125-130°C (Sarıışık, 2001).

Scouring

Baking is the process of removing impurities contained in cotton products by treating them in hot dilute sodium hydroxide solution. During the cooking process, impurities other than colorants become removed by washing. (Çiftci and Çiftci, 1991). With the baking process, impressive improvements are observed in the wettability and absorbency properties of natural fibers, while a 5-10% loss in weight is observed. This weight loss results from the degradation of proteins into amino acids, the transformation of pectates into soluble sodium salts, the degradation of hemicelluloses and the degradation of cellulose (Shore, 1995).

The term “cooking” actually refers to the kier boiling process, which is a batch process. Boilers are low-pressure open to the atmosphere or closed, high-pressure boilers (autoclaves) that can operate at temperatures above 100 °C. The product fed to the boiler in the form of a rope is processed with 2% NaOH solution for 8-12 hours in open boilers under atmospheric pressure, or for 6-8 hours at 125-130°C in closed boilers under pressure (Çiftci and Çiftci, 1991).

Bleaching of Cotton

Cotton contains natural coloring substances. The purpose of the bleaching process is to obtain white fabrics by eliminating these coloring substances with the help of bleaching agents. Chemical bleaching of textile fibers is further enhanced by the addition of optical brightener (Karmakar, 1999). We can list three basic methods

of classical bleaching. These are bleaching with sodium hypochlorite, bleaching with sodium chlorite and bleaching with hydrogen peroxide.

RESULTS

In the textile industry, pre-treatment has a very important place in order to make the fabric ready for dyeing and printing. Pre-treatment of fabrics containing cotton raw material is very important due to some of their properties. Due to cotton fabrics' features such as good washing properties, strength and abundance, it is necessary to be more careful in pre-treatment processes in the textile industry.

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BÖLÜM 4

BIOSORPTION OF DYE FROM SYNTHETIC WASTEWATER USING CHITOSAN NANOPARTICLES AND LOW-DENSITY POLYETHYLENE (CHNP/LDPE) BIOCOSMPOSITE AS ADSORBENT

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Ransome Olaoye Opeyemi

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1.0 INTRODUCTION

The advent of industrialization marks a pivotal advancement in technological progress and civilization. However, the generation of waste presents significant environmental challenges that must be mitigated to minimize ecological harm [1]. Industrial, domestic, and chemical processes produce waste, often toxic and detrimental to ecosystems. Waste is typically categorized as either solid (refuse) or liquid (wastewater/sewage), with wastewater being the more prevalent and impactful due to its contaminant concentration. Consequently, proper treatment is essential before disposal into water bodies, the primary endpoints for waste discharge [2, 3]. Dyes are a common component of industrial and chemical processes, characterized by their stability which complicates the treatment of extensively dispersed and azo dyes. Numerous factories use synthetic dyes and pigments, which often end up in natural waterways [4]. Reactive dyes, chosen for their

vibrant colors and ease of use, are classified as anionic or cationic. Despite their advantages, many reactive dyes are toxic to organisms, posing risks to aquatic ecosystems. The accumulation of dyes in wastewater from industries such as textiles, paper, rubber, and plastics significantly contributes to water pollution [5]. The inadequate treatment of colored wastewater can lead to elevated chemical oxygen demand (COD) and increased overall toxicity in aquatic environments [6].

Various methods exist for wastewater treatment, including physical, biological, and chemical approaches [7]. Effective pollutant removal typically involves a combination of physicochemical and biological techniques. Research continues to seek cost-effective and efficient treatment combinations, including solvent extraction, adsorption, filtration, oxidation, electrochemical treatment, membrane separation, ion exchange, advanced oxidation, adsorption onto unconventional solids, biomass utilization, nanofiltration, and biosorption [8,9,10]. This study focuses on the biosorption technique which refers to the process by which biological materials, such as bacteria, algae, fungi, or plant biomass, adsorb and accumulate heavy metals or other contaminants from aqueous solutions. This process relies on the natural affinity of the biological material's surface for binding with metal ions or pollutants, often through mechanisms like ion exchange, complexation, and micro-precipitation. Biosorption is particularly useful for removing toxic metals from wastewater and is considered an eco-friendly and cost-effective method for environmental remediation [38]. Biosorption offers numerous benefits, such as selective metal

extraction over a wide range of pH levels and temperatures, rapid adsorption/desorption kinetics, and cost-effectiveness. Biosorption depends on the availability of biosorbents/adsorbents. Biological materials used to accumulate and concentrate pollutants from aqueous solutions are termed "bioadsorbents [11]." Examples include activated carbon, sawdust, silica gel, peat, hay, vegetable fibers, straw, feather, sand, clay, and wool.

Bioplastics, derived from renewable biomass sources like corn starch, vegetable fats, sawdust, woodchips, and straws, offer an alternative to conventional plastics made from fossil fuels. Many bioplastics are based on cellulose, a plant-derived polysaccharide. Research by the Wyss Institute suggests chitosan, a viable bioplastic, could replace traditional plastics in various applications due to its adsorbent/biosorbent properties [12]. Low-Density Polyethylene (LDPE), although primarily petrochemical-based and non-biodegradable, can also be biobased and contain renewable carbon.

This study aims to utilize Low-Density Polyethylene and Chitosan Nanoparticles in the biosorption process to treat synthetic wastewater containing dye contaminants [13,14,15]. The adsorbent properties of chitosan and polyethylene will be examined in the biosorption of Congo red and Bromocresol green dyes. The efficiency of this biosorption process will be evaluated to establish it as a reliable wastewater treatment method. The assessment will consider parameters such as pH, contact time, initial dye concentration, and temperature [6,17]. Additionally, adsorption isotherms, kinetics, and thermodynamic parameters will be evaluated and reported.

2.0 MATERIALS AND METHODS

2.1 MATERIALS

All chemicals used in this study were of analytical grade and utilized without further purification. The Congo red dye, Bromocresol Green dye, hydrochloric acid, sodium hydroxide, distilled water, buffer solution (pH 7.0), acetic acid, and xylene were sourced from the Physical and Environmental Chemistry Laboratory. Distilled water was used to prepare all solutions. All chemicals, including the Congo red dye and Bromocresol Green dye, were obtained from Sigma-Aldrich UK.

2.1.1 PREPARATION OF LOW-DENSITY POLYETHYLENE-CHITOSAN NANOPARTICLES BIOCOMPOSITE

The biocomposite synthesis of Low-Density Polyethylene and Chitosan Nanoparticles (LDPE/CHNP) was carried out by adapting the solvent casting technique described by Choi [7], as characterized in our prior research by Adelaja et al. [1]. First, low-density polyethylene (LDPE) pellets were dissolved by reflux heating in 50 mL of xylene, while chitosan nanoparticles (CHNP) were dissolved in 10 mL of 0.02 M acetic acid. These solutions were then gradually combined in specified ratios and stirred at 100 rpm to form a viscous mixture. The mixture was cooled to 37°C, spread onto a stainless-steel plate, and cast. The composite was then dried in a vacuum oven (VWR, UK) at 35°C to remove all residual solvents. Once thoroughly dried, the films were kept

in a moisture-free environment, finely ground, and stored in an airtight container.

2.1.2 PREPARATION OF CONGO RED DYE AND BROMOCRESOL GREEN STOCK SOLUTION

A 1000 mg/L of Congo Red dye solution and Bromocresol green was prepared by dissolving 1g each of Congo red and Bromocresol green in 1000 mg/L of distilled water using a 1000 mL standard flask

2.2 Experimental Design for Adsorption of Congo Red Dye, Bromocresol Green Dye, and Their Binary Mixture

A batch biosorption experiment was conducted using Low-Density Polyethylene-Chitosan Nanoparticles (LDPE/CHNP) to assess their adsorption capacity for Congo Red and Bromocresol Green dyes, both individually and in binary mixtures at concentrations of 10, 20, 30, 40, and 50 mg/L. The adsorbent (0.01 g) was added to six containers, each receiving 1.2 mL of a 30 mg/L Congo Red dye solution, 1.2 mL of Bromocresol Green dye solution, and diluted to 40 mL with deionized water. The pH of the mixtures was adjusted from 4.0 to 9.0 using 0.1 M hydrochloric acid and 0.1 M sodium hydroxide. Agitation was performed at 150 rpm for 30 minutes using an orbital shaker (Fischer Scientific Inc., UK). Post-agitation, the solutions were filtered, and the optical density of the filtrates was measured at 492 nm and 616 nm for Congo Red and Bromocresol Green dyes, respectively, using a UV-visible spectrophotometer.

Furthermore, the impact of varying initial concentrations (15, 30, 45,

60, and 75 mg/L) of Congo Red and Bromocresol Green dyes in binary mixtures was investigated. Each experiment involved adding 0.01 g of LDPE/CHNP to labeled beakers containing 1.2 mL of Congo Red dye solution, 1.2 mL of Bromocresol Green dye solution, and adjusting to 40 mL with distilled water. Optimal pH levels were achieved with 0.1 M HCl and 0.1 M NaOH, followed by agitation for 90 minutes on an orbital shaker. After agitation, the samples were filtered, and the filtrates were analyzed at 492 nm and 616 nm wavelengths for Congo Red and Bromocresol Green dyes, respectively.

Additionally, adsorption kinetics were investigated by adding 0.01 g of LDPE/CHNP to five separate beakers containing 1.5 mL each of Congo Red and Bromocresol Green dye solutions (75 mg/L), adjusted to 40 mL with distilled water. pH adjustment was performed, followed by agitation for 15, 30, 60, 90, and 120 minutes on an orbital shaker. Post-agitation, the samples were filtered, and the resulting filtrates were analyzed using UV-visible spectrophotometry at 492 nm and 616 nm for Congo Red and Bromocresol Green dyes, respectively. However, to study temperature effects, 0.01 g of LDPE/CHNP was placed in a beaker with 1.5 mL each of Congo Red and Bromocresol Green dye solutions, adjusted to 40 mL with distilled water. The samples were immersed in a water bath at temperatures ranging from 30°C to 70°C for 90 minutes. After filtration, UV-visible spectrophotometry was used to analyze the filtrates at 492 nm and 616 nm for Congo Red and Bromocresol Green dyes, respectively.

2.3 ADSORPTION ISOTHERMS

For this study, equilibrium analysis utilized Langmuir and Freundlich isotherms. The linearized Langmuir equation (Equation 1) is expressed as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad 1$$

In this context, Q_e (mg/g) represents the maximum adsorption capacity at equilibrium, Q_o (mg/g) denotes the monolayer capacity of the adsorbent, and b (L/mg) signifies the constant related to adsorption energy. C_e (mg/L) stands for the equilibrium dye concentration. A linear relationship between C_e/Q_e and C_e indicates adherence to the Langmuir model, facilitating determination of Q_o and b .

The linearized Freundlich equation (Equation 2) is expressed as:

$$\log_{qe} = \log_{K_F} + \frac{1}{n} \log_{C_e} \quad 2$$

Here, K_F (mg/g) represents the Freundlich constant specific to the system, and n (dimensionless) characterizes the intensity of adsorption. A linear relationship between $\log_{(Q_e)}$ and $\log_{(C_e)}$ indicates conformity to the Freundlich model, aiding in determination of K_F and n .

2.4 ADSORPTION KINETIC STUDIES

To characterize the experimental data for the estimation of rate constants, the pseudo-first order and pseudo-second-order models were used in this study [2].

2.4.1 PSEUDO FIRST ORDER AND PSEUDO SECOND ORDER MODEL

The linearized pseudo-first-order equation can be represented by the following Equation 3:

$$\begin{aligned} & \ln(q_e - q_t) \\ & = \ln q_e \\ & - k_1 t \end{aligned} \tag{3}$$

Here, k_1 (min^{-1}) represents the rate constant for pseudo-first-order adsorption. Q_e and q_t denote the amount adsorbed per unit mass of adsorbent at equilibrium and at time t , respectively. A linear relationship when plotting $\ln(Q_e - q_t)$ against t suggests adherence to pseudo-first-order kinetics.

The linearized form of the Lagergren pseudo-second-order kinetic equation (Equation 4) is:

$$\begin{aligned} & \frac{1}{t} \\ & = \frac{1}{k_2 q_e^2} \\ & + \frac{1}{q_e} X t \end{aligned} \tag{4}$$

Here, k_2 ($\text{g}/(\text{mg} \cdot \text{min})$) represents the rate constant for pseudo-second-order kinetics. A linear relationship when plotting $1/t$ against t indicates conformity to pseudo-second-order kinetic behaviour.

3.0 RESULTS AND DISCUSSION

3.1 EFFECT OF PH ON THE ADSORPTION OF CONGO RED AND BROMOCRESOL GREEN IN THEIR BINARY MIXTURE

The pH level of a solution is a significant factor in the process of dye biosorption, impacting both the surface charge of the adsorbent and the configuration of the adsorbate molecules. Within this investigation, the influence of the initial pH on dye adsorption within a binary system was examined over a pH range spanning from 4 to 9. As depicted in Figure 1, the absorption percentage of Congo Red (CR) rose from pH 4 to 5, reaching its maximum at pH 5, and subsequently decreased gradually from pH 5 to 9, resulting in a 66% dye absorption. Likewise, Bromocresol Green (BG) exhibited maximal adsorption at pH 5, followed by a gradual decrease with the escalation of pH up to 8. Amid pH 8 and 9, there was a minor rise in absorption from 84% to 85%. Notably, the quantity of BG absorbed surpassed that of CR, notably at pH 4, where BG absorption reached 96% compared to CR's 72%. The decline in adsorption efficacy at elevated pH levels can be ascribed to the enlargement of negatively charged binding sites, instigating electrostatic repulsion on the negatively charged surface of the adsorbent, thereby impeding the adsorption of the anionic Bromocresol Green dye [21, 22, 23]

The uniformity in the outcomes can be associated with the characteristics of chitosan, the employed adsorbent, which demonstrates an augmentation in its negatively charged surface with increasing pH levels. Once the pH of the solution surpasses the Point Zero Charge (pH_{Zc}), the adsorbent's surface assumes a negative charge,

thereby amplifying the uptake of cationic dyes. Conversely, when the solution's pH drops below the pHzc, the adsorbent's surface becomes positively charged, rendering it more favorable for adsorbing anionic dyes. Notably, chitosan possesses a pHzc of 6.3. Intriguingly, the highest proportion of absorbed dye for CR was observed at pH 5, a value below the pHzc. This occurrence is linked to the adsorbent's surface acquiring a positive charge, which facilitates the adsorption of the anionic dye (CR) [24].

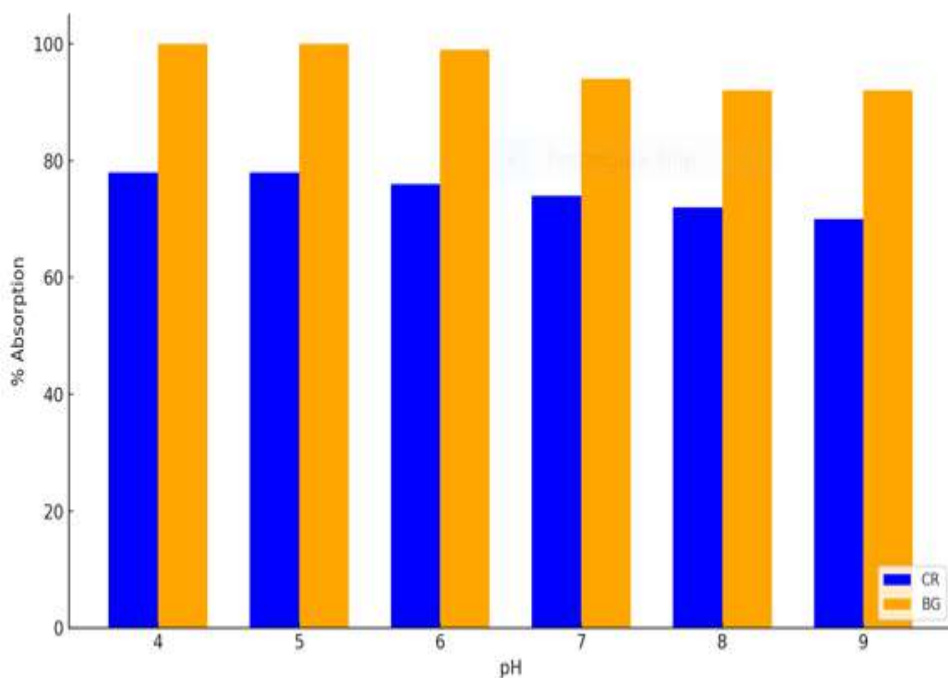


Figure 1: Effect of pH on LDPE/CHNP Adsorption of CR and BG (Initial Conc. 30 mg/L, 150 rpm, 30 min, 0.01 g Adsorbent)

3.1.1 EFFECT OF CONTACT TIME ON THE ADSORPTION OF CONGO RED AND BROMOCRESOL GREEN DYE IN THEIR BINARY MIXTURE

The effect of contact time is a crucial factor to consider when determining the optimal duration for dyes to adsorb onto an adsorbent, particularly in industrial contexts [25]. It serves as a key parameter for ensuring the practical application of adsorbents. A desirable adsorbent should exhibit a rapid adsorption rate. In this study, the effect of contact time was investigated by employing different time intervals while keeping the adsorbent dose and initial dye concentration constant. The impact of contact time on the binary mixture of Congo red dye and Bromocresol green dye was examined, with the results depicted in Fig 2.

Initially, the adsorption process demonstrated rapid kinetics, followed by a gradual decrease until reaching an equilibrium state. Beyond this equilibrium point, the sorption rate remained constant. This equilibrium state was typically achieved around 90 minutes, a timeframe selected for this study to ensure optimal adsorption and the attainment of equilibrium [26,27]. The swift initial adsorption can be attributed to the abundance of available active sites on the adsorbent. The rapid initial sorption is primarily governed by the diffusion process from the bulk solution to the surface of the adsorbent. As active sites become less accessible and eventually reach saturation at equilibrium, the sorption process is likely controlled by attachment in the later stages [28].

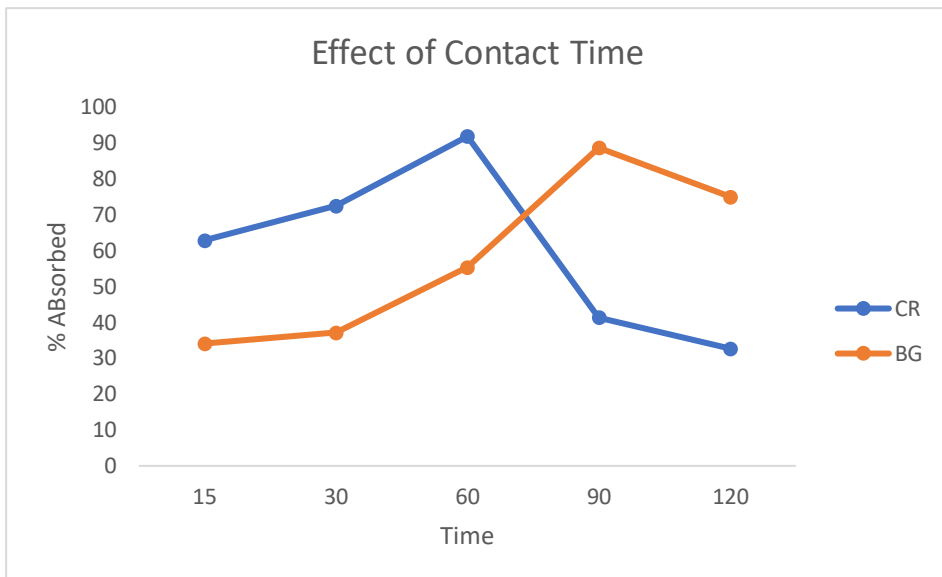


Figure 2: pH Impact on Congo Red and Bromocresol Green Biosorption using LDPE/CHNP

(Initial Conc.: 30 mg/L, Agitation Speed: 150 rpm, Adsorbent Dosage: 0.01 g, pH: 9)

3.1.2 EFFECT OF INITIAL CONCENTRATION ON THE ADSORPTION OF CONGO RED AND BROMOCRESOL GREEN IN THEIR BINARY MIXTURE

Fig. 3 illustrates the relationship between adsorption efficiency and initial concentration. As shown in the figure, increasing the initial dye concentration results in higher adsorption until equilibrium is reached. For both CR and BG, raising the initial concentration from 15 mg/L to 75 mg/L led to an increase in q (measured in mg/g) from 14.97 mg/g to 24.65 mg/g. Similarly, for BG, increasing the initial concentration from 15 mg/L to 75 mg/L resulted in an increase in q from 12.20 mg/g to 24.48 mg/g.

This linear correlation between initial dye concentration and adsorbed dye amount is due to the increased concentration overcoming mass transfer barriers between the liquid and solid phases, facilitating effective adsorption. Thus, in this study, the quantity of dye adsorbed onto the biosorbent increased with escalating initial dye concentration, driven by a heightened concentration gradient that aided in overcoming mass transfer barriers and enhancing equilibrium sorption until saturation was reached [29,30].

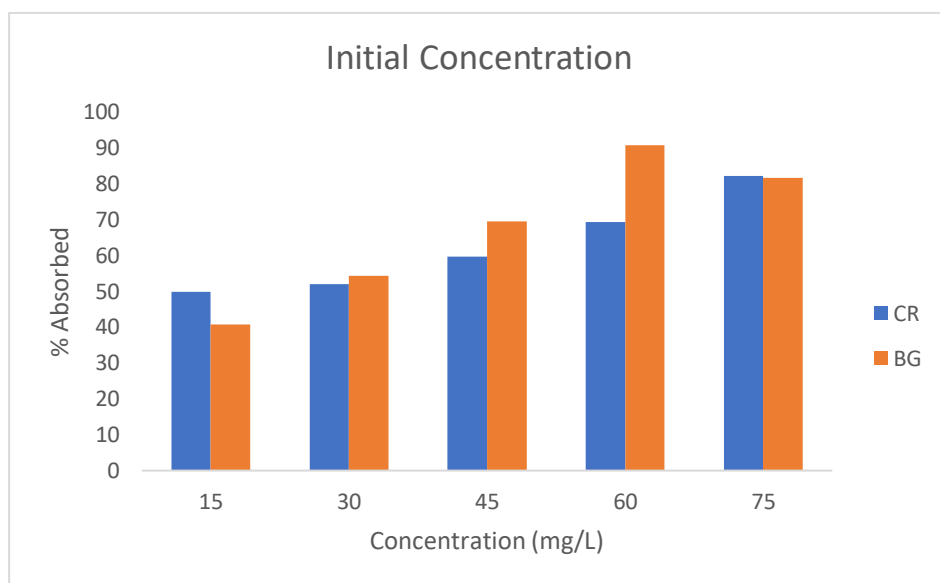


Figure 3: Impact of Initial Concentration on LDPE/CHNP Biosorption of Congo Red and Bromocresol Green Dyes (pH 9.0, 150 rpm, 90 min, 0.01 g Adsorbent)

3.1.3 EFFECT OF ADSORBENT DOSAGE ON ADSORPTION OF CONGO RED AND BROMOCRESOL GREEN DYE IN THEIR BINARY MIXTURE

The findings indicated that augmenting the adsorbent dose resulted in a proportional rise in the percentages of dye removal efficiency. This can be attributed to the expanding surface area of the adsorbent and the increased availability of adsorption sites. As the adsorbent dose was enhanced, there was a corresponding increase in the removal efficiency of both CR and BG. Consequently, the amount of adsorbed dye also exhibited an upward trend [31,32].

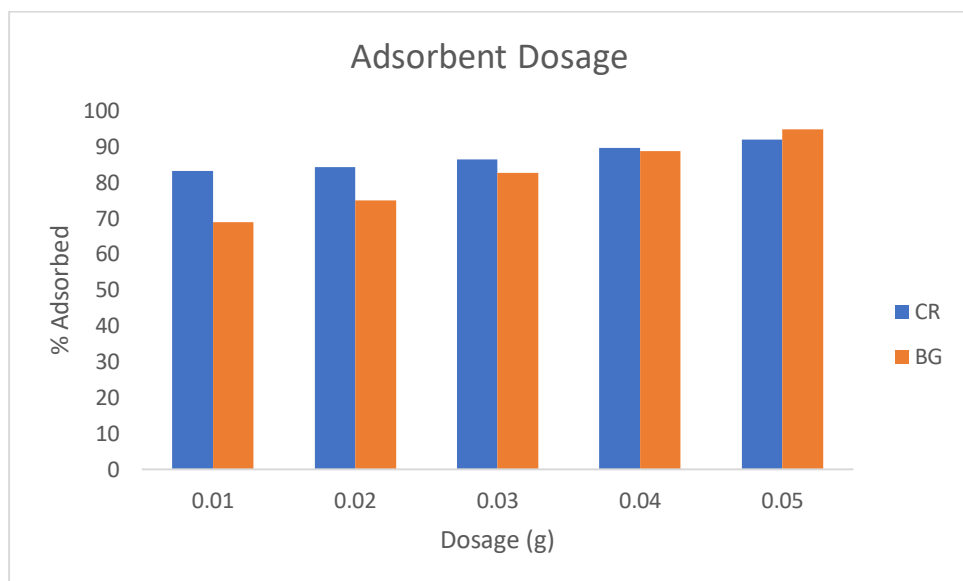


Figure 4: Adsorbent Dose Effect on Congo Red and Bromocresol Green Biosorption (pH 9.0, 150 rpm, 90 min, 0.01 g to 0.05 g LDPE/CHNP)

3.1.4 EFFECTS OF TEMPERATURE ON THE ADSORPTION OF CONGO RED AND BROMOCRESOL GREEN DYE IN THEIR BINARY MIXTURE

Temperature's impact on adsorption is a critical factor in determining the thermodynamic conditions of the process, whether it is endothermic or exothermic. In this study, temperature's effect was assessed over a

range of 303 K to 343 K while keeping other parameters constant [17,33]. From Fig. 5, it is evident that as temperature increases, adsorption decreases uniformly for both CR and BG from 303 K to 323 K. However, from 323 K to 343 K, adsorption slightly increases but does not reach the level observed at 303 K. This aligns with the principle that adsorption decreases as temperature rises, with molecules desorbing from the surface at higher temperatures. This phenomenon may be attributed to the contraction and alteration of active sites on the adsorbent at elevated temperatures, leading to a decrease in available active surface. Additionally, at higher temperatures, the larger separation between dye molecules and the adsorbent could result in dye leaching into the solution [34]. This suggests that the adsorption of both CR and BG is an exothermic process, favoring lower temperature solutions.

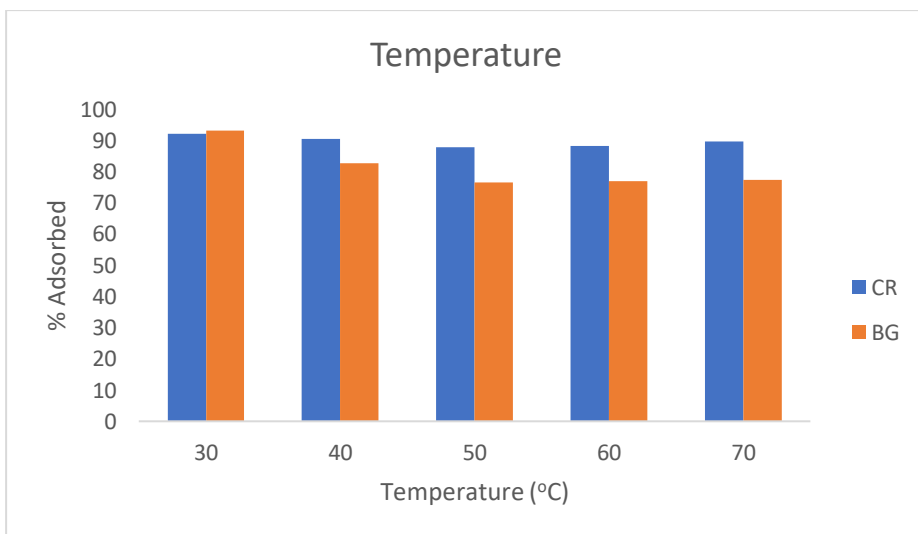


Figure 5: Temperature Effect on Biosorption of Congo Red and Bromocresol Green Dyes in Binary Mixture using LDPE-CHNP (pH 9.0, 150 rpm, 90 min, Initial Conc. 30 mg/L, Adsorbent Dosage 0.01 g)

3.1.5 THERMODYNAMICS STUDY OF THE ADSORPTION OF CONGO RED AND BROMOCRESOL GREEN IN THEIR BINARY MIXTURE

Investigating the temperature dependency of adsorption reactions sheds light on enthalpy and entropy alterations, aiding in discerning whether the process is exothermic or endothermic.

Thermodynamic parameters (ΔG , ΔH , and ΔS) for Congo Red (CR) and Bromocresol Green (BG) adsorption in the binary system were derived from Van't Hoff plots (Table 1), where negative ΔG values indicate the process's feasibility and spontaneity (Table 1).

Positive ΔH values denote an endothermic adsorption, while negative ΔS values imply a reduction in system disorder upon dye absorption [35, 36].

With rising temperature, the ΔG value becomes increasingly negative, rendering adsorption more favorable.

The similarity in ΔG values for CR and BG stems from their shared characteristics as anionic dyes.

Despite the endothermic nature of the process, the high spontaneity observed in the binary system for both dyes suggests their adsorption onto the LDPE/CHNP biocomposite is complementary rather than competitive [37].

Table 1: Table of the thermodynamic parameters of the Biosorption of Congo red and Bromocresol green dye in their binary mixture using LDPE/CHNP.

Thermodynamics Parameters	ΔG	ΔG
$\Delta G(\text{kJmol}^{-1})$	Congo Red	Bromocresol green
303	-6.167	-6.587
313	-5.877	-4.048
323	-5.422	-3.309
333	-5.477	-3.316
343	-5.418	-3.368
$\Delta S (\text{JK}^{-1}\text{mol}^{-1})$	-19.58	-75.44
$\Delta H(\text{KJmol}^{-1})$	11.99	28.49

3.2 ADSORPTION ISOTHERM OF THE ADSORPTION OF CONGO RED AND BROMO CRESOL GREEN DYE IN THEIR BINARY MIXTURE

The Langmuir model, which represents a monolayer homogeneous adsorbent surface, and the Freundlich model, corresponding to a heterogeneous adsorbent surface, are commonly employed in adsorption investigations. In this experiment, the isothermal data were evaluated using Langmuir and Freundlich isotherm expressions. As depicted in Fig. 6, the C_e/Q_e versus C_e plot adheres to the Linearized Langmuir equation. The high correlation coefficients (R^2) for CR and BG within the binary system, recorded as 0.9965 and 0.9989, respectively (Table 2), indicate a strong correlation close to 1. This validates the compatibility of dye adsorption onto the LDPE/CHNP adsorbent with the Langmuir

isotherm, suggesting a monolayer homogeneous adsorption process [18, 39].

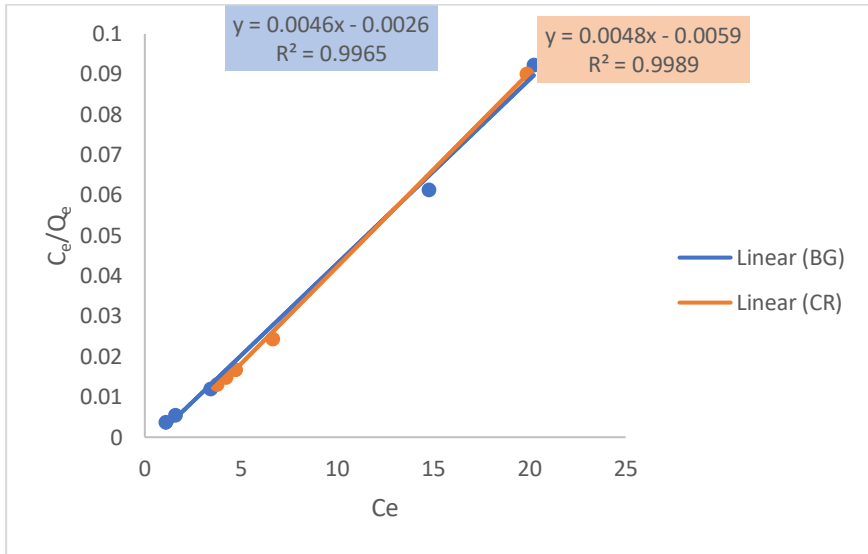


Figure 6 Langmuir Isotherm for the Biosorption of Congo red and Bromocresol green dye in their binary mixture using LDPE/CHNP (Adsorbent dosage = 0.01 g, Temperature = 300 K, agitation speed = 150 rpm, Contact Time = 15,30,45,60,75 minutes)

Table 2 Parameters of Langmuir Isotherm

Parameters	Q_0 (mg/g)	b (L/mg)	R_L	R^2
CR	208.33	0.813	0.039	0.9989
BG	217.39	1.769	0.018	0.9965

The adsorption capacity, denoted as Q_0 , signifies the maximum adsorption level corresponding to complete monolayer coverage. In

this scenario, the mass capacity of the biocomposite for CR and BG within their binary mixture was determined to be 208.33 and 217.39, respectively. Both dyes demonstrate an RL value below 1, indicating a favorable adsorption process.

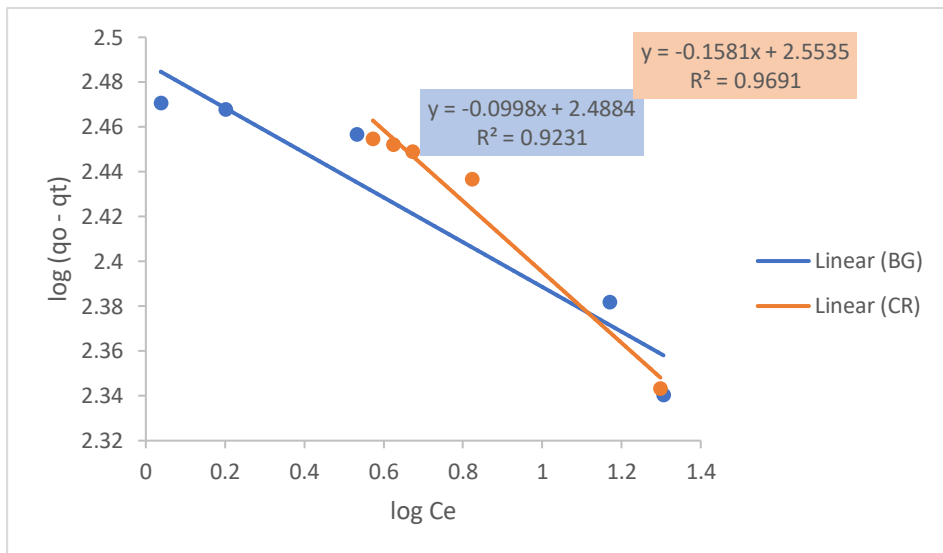


Figure 7 Freundlich Isotherm for the Biosorption of Congo red and Bromocresol green dye in their binary mixture using LDPE/CHNP (Adsorbent dosage = 0.01 g, Temperature = 300 K, agitation speed = 150 rpm, Contact Time =15,30,45,60,75minutes)

Table 3 Parameters of Freundlich Isotherm

PARAMETERS	$K_F(\text{mg/g})(\text{mg/L})$	N	R^2
CR	12.85	-6.325	0.9691
BG	12.04	-10.02	0.9231

In the linearized Freundlich adsorption model shown in Fig. 7, where $\log Q_e$ is plotted against $\log C_e$, the adsorption behavior of CR and BG onto the adsorbent conforms to the Freundlich isotherm model under the experimental conditions.

The R^2 values for the binary system are 0.9691 and 0.9231 for CR and BG, respectively (Tab. 3). With n values for both dyes less than 1 (Tab. 3), it suggests a chemical process governs the biosorption of the dyes onto the biosorbent.

The utilization of the Freundlich and Langmuir isotherms on the dyes hints at the potential presence of varied surface conditions on the biosorbent, indicating monolayer adsorption.

Consequently, this suggests that the adsorption of the dyes predominantly involves chemisorption [40].

3.3 ADSORPTION KINETICS OF THE ADSORPTION OF CONGO RED AND BROMOCRESOL GREEN DYE IN THEIR BINARY MIXTURE

Among the commonly utilized kinetic models, including the Lagergren pseudo-first-order, Lagergren pseudo-second-order, and intraparticle diffusion models, the experimental results (Fig. 8) clearly indicate that the pseudo-first-order model did not align well, as evidenced by an R^2 value below 0.99.

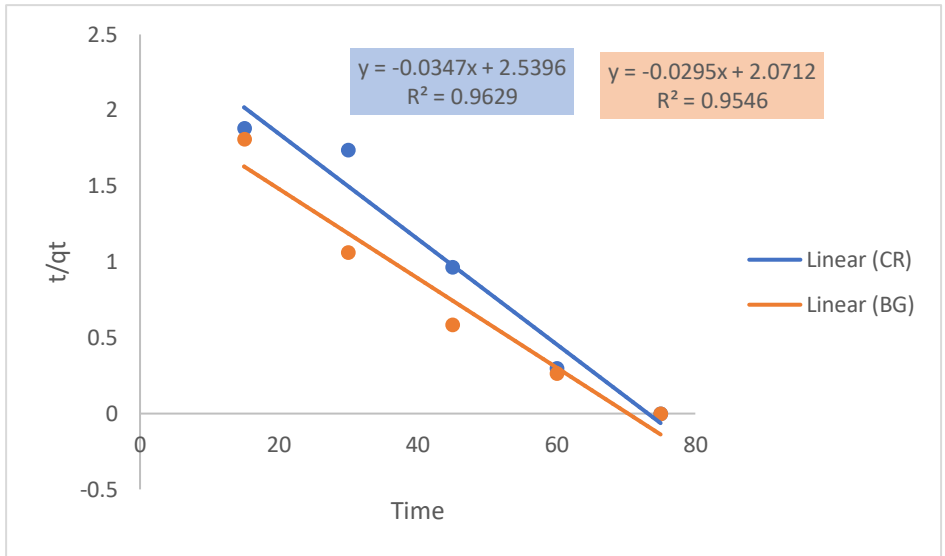


Figure 8 Pseudo first order kinetics for the Biosorption of Congo red and Bromocresol green dye in their binary mixture using LDPE/CHNP (Adsorbent dosage = 0.01 g, agitation speed = 150 rpm, contact time: 15, 30, 45, 60, 75minutes)

The projected and observed Q_e values display a lack of agreement, suggesting that the adsorption process of the two dyes in their binary mixture onto LDPE/CHNP does not adhere to first-order kinetics. This deduction is supported by the outcomes of Ashoka and Inamdar's [6] research, which dealt with the adsorption removal of methyl red from aqueous solutions using processed sugarcane bagasse and activated carbon.

PSEUDO SECOND ORDER KINETICS

Kinetic modelling of CR and BG adsorption onto LDPE/CHNP followed a Lagergren pseudo- second-order model (Fig. 9).

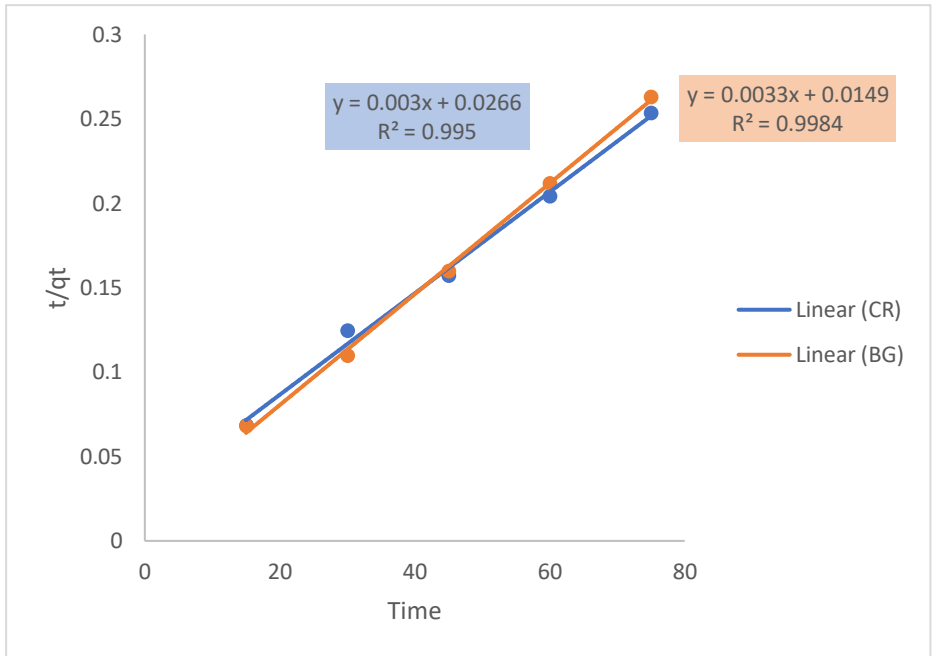


Figure 9 Pseudo Second-Order kinetics for the Biosorption of Congo red and Bromocresol green dye in their binary mixture using LDPE/CHNP (Adsorbent dosage = 0.01 g, agitation speed = 150 rpm, contact time: 15, 30, 45, 60, 75 minutes)

As depicted in Fig. 9, it becomes evident that the pseudo-second-order reaction aligns effectively, as indicated by an R2 value exceeding 0.99. In this model, the rate-limiting phase is surface adsorption, a process encompassing chemisorption.

This mechanism involves the elimination of a solute through physicochemical interactions between the two phases [41].

Table 4: Kinetics Study on the Biosorption of Congo red and Bromocresol green dye in their binary mixture using LDPE/CHNP as adsorbent

Parameters	Pseudo First Order		Pseudo Second Order		
	K_1	R^2	K_2	Q_e (mg/g)	R^2
CR	0.08	0.9629	0.00034	333.33	0.995
BG	0.068	0.9546	0.00073	303.03	0.9984

According to Table 4, the equilibrium adsorption capacities (Q_e) for Congo Red (CR) and Bromocresol Green (BG) in their binary system were found to be 333.33 mg/g and 303.33 mg/g, respectively. The comparison between calculated and experimental Q_e values shows a strong agreement with the Pseudo-second-order model, as indicated by a correlation coefficient (R^2) exceeding 0.99 [6].

This suggests that the Pseudo-second-order model more accurately represents the adsorption kinetics for CR and BG in their binary system compared to the Pseudo-first-order model. The reduction in Q_e values for both dyes in the binary system may be due to competition for accessible adsorption sites on the adsorbent [33]. Previous studies on the adsorption of methyl red (MR) onto adsorbents also align with Pseudo-second-order kinetics, diverging from Pseudo-first-order kinetics. The adsorption mechanism for anionic dyes by chitosan involves the protonation of chitosan's amino groups in the presence of

H⁺. In an aqueous solution, the anionic dye dissolves, and sulfonate groups in acid or reactive dyes dissociate to form anionic dye ions, leading to adsorption through electrostatic attraction of these ions. As noted by Yeşim and Başak [43], the presence of multiple components such as metal ions or dyes in a solution induces competition for adsorption sites, thus enhancing the total adsorption capacity of the adsorbent.

Due to the similar ionic characteristics of CR and BG, their simultaneous adsorption in the LDPE/CHNP system is competitive. These dyes readily interact with the same active sites on the adsorbent, which could explain the closely aligned adsorption efficiencies observed in the binary system [42-43]. Many studies have been conducted for the characterization of wastewater, methods for treatment efficiency are being studied [44-45].

4.0 CONCLUSION

This study focused on assessing the effectiveness of Low-Density Polyethylene/Chitosan Nanoparticle (LDPE/CHNP) adsorbents for the concurrent removal of specific dyes, such as Congo red and Bromocresol green. The investigation delved into adsorption equilibrium using Langmuir and Freundlich isotherms. The outcomes indicated a stronger alignment with the Langmuir model, suggesting a greater propensity for chemisorption rather than physisorption. Kinetics exploration encompassed both pseudo-first-order and pseudo-second-order models. Within the context of a binary system, nanoparticles were utilized as adsorbents for the adsorption of CR and

BG. Thermodynamic analysis disclosed an exothermic reaction with a negative Gibbs free energy (ΔG), underscoring the feasibility and spontaneity of the process. Due to the similar charges of the two dyes and their capacity to interact freely with distinct active sites on the adsorbent, their competitive adsorption effectiveness was noted within the binary system.

AUTHOR'S CONTRIBUTION

Author O. A. A. conceptualized the research and supervised the research, R.O. O. and O.E. A. carried out experimental work, collated data and prepared the manuscript. All authors reviewed and approved the final version of the manuscript,

CONFLICT OF INTERESTS

The Authors also declare that there are no conflicts of interests or competing interests.

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BÖLÜM 5

ENVIRONMENTAL IMPACTS OF BIO-BASED POLYMER MATRICES AND RECYCLED FIBERS: A COMPREHENSIVE ANALYSIS WITHIN KPK, PAKISTAN

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Irfan Mateen

Abbas Ali

Mansoor Ali Khan

INTRODUCTION

In the 21st century, global environmental challenges pose unprecedented threats to ecosystems, human health, and global stability. Climate change, driven by anthropogenic activities such as greenhouse gas emissions from fossil fuels and deforestation, stands out as a critical issue (IPCC, 2021). This phenomenon leads to escalating global temperatures, sea-level rise, altered precipitation patterns, and more frequent extreme weather events (IPCC, 2021) [1].

Alongside climate change, environmental degradation worsens due to resource depletion and pollution. Overexploitation of minerals, forests, and freshwater jeopardizes biodiversity and essential ecosystem services (UNEP, 2022). Pollution from industrial emissions,

agricultural runoff, and plastic waste contaminates air, water, and soil, posing significant health risks worldwide (UNEP, 2022) [2].

Materials science plays a crucial role in addressing these complex challenges by developing innovative materials aimed at reducing environmental impacts across sectors such as construction, transportation, energy, and consumer goods. Sustainable materials, including bio-based polymers, recycled metals, and composite materials, integrate principles of resource efficiency, longevity, and minimal environmental impact throughout their life cycles (Gupta & Singh, 2020) [3].

Composite materials, combining two or more materials to achieve specific mechanical, thermal, or chemical properties, play a pivotal role in advancing sustainability goals (Zweben & Schwartz, 2009) [4]. Incorporating bio-based or recycled components allows composites to reduce reliance on virgin resources, lower carbon footprints, and extend product lifecycles through enhanced durability and performance (Garcia-Lopez et al., 2021). Applications span from lightweight automotive parts to energy-efficient building materials, significantly contributing to resource conservation and environmental protection across industries (Garcia-Lopez et al., 2021) [5].

The primary objective of this research is to investigate the development of sustainable composite materials using bio-based or recycled components. The study aims to evaluate the feasibility and

effectiveness of integrating these materials into composite matrices, analyzing their environmental impacts throughout their lifecycle—from production and use to disposal. Additionally, the research seeks to assess these materials' potential to mitigate environmental degradation by reducing carbon emissions, conserving natural resources, and minimizing waste generation.

Focused on the Khyber Pakhtunkhwa (KPK) region, the scope of this research includes a variety of materials such as bio-based polymers, recycled fibers, and other sustainable components used in composite materials. Applications will be explored in environmental contexts relevant to KPK, including construction materials, automotive components, packaging, and consumer goods. This localized perspective aims to highlight regional sustainability practices and challenges specific to the area.

Academically, this study contributes to materials science and environmental sustainability by innovatively exploring the use of bio-based and recycled materials in composite formulations. It addresses existing gaps in understanding the environmental performance of sustainable composites and their potential contributions to global sustainability targets. The research introduces new methodologies for assessing the sustainability of these materials, advancing both theoretical insights and practical applications.

Practically, findings from this research are poised to inform industries, policymakers, and environmental advocates within KPK. Insights into developing and adopting sustainable composite materials can guide local manufacturers in selecting eco-friendly materials and processes, thereby enhancing corporate sustainability strategies. Recommendations for integrating these materials into regulatory frameworks can promote environmental stewardship and drive green innovation in regional manufacturing practices. Additionally, understanding the environmental benefits of sustainable composites empowers local advocacy groups and consumers to make informed choices that support sustainable consumption and production patterns.

In conclusion, this research provides valuable guidance on selecting materials that offer superior environmental performance without compromising product quality or performance.

It also offers strategies for optimizing manufacturing processes to reduce energy consumption, waste generation, and environmental footprint, thereby influencing environmental policies related to sustainable materials, circular economy principles, and climate action initiatives.

2. Material and Methods:

2.1 Investigation sites:

2.1.1 Industrial Areas in Peshawar

The investigation was conducted in Peshawar, the capital city of Khyber Pakhtunkhwa province in Pakistan, located at 34.0151° N latitude and 71.5249° E longitude. Peshawar experiences a semi-arid climate, characterized by hot summers with temperatures often exceeding 40°C, and mild winters with temperatures rarely dropping below 4°C. The annual rainfall averages around 400 mm, predominantly occurring during the monsoon season from July to September. The city's soil primarily consists of alluvial deposits, supporting diverse agricultural activities, yet susceptible to erosion and compaction.

Peshawar's topography and rapid urbanization contribute to increased vulnerability to climate change impacts, making it a critical area for resilience research. The city has several industrial areas where bio-based polymers and recycled fibers could be sourced and tested. Industries here could provide essential data on the current use of materials and waste management practices. This site offers a rich source of real-world data on industrial practices and material applications, critical for evaluating the feasibility and effectiveness of sustainable composites in an industrial setting.

2.1.2 Educational and Research Institutions

The study also involved collaboration with universities and research centers in KPK, such as the University of Peshawar and CECOS University. These institutions facilitated laboratory testing, material characterization, and collaborative research. They provided a platform for engaging with experts and students in the field of materials science and environmental studies. Access to advanced research facilities and academic resources was invaluable for conducting detailed material analysis and experimental validation.

2.1.3 Local Recycling Facilities

Recycling plants and waste management facilities within KPK were crucial for sourcing recycled fibers and understanding current recycling practices. These facilities offered practical insights into the feasibility of integrating recycled materials into composite production. Observing and collaborating with these facilities helped in assessing the quality, availability, and processing methods of recycled materials, which is crucial for developing sustainable composites.

The combination of these selected sites offers a comprehensive yet focused investigation ground for evaluating the feasibility, effectiveness, and environmental impact of sustainable composite materials in the KPK region. Each site plays a crucial role in the



Figure 1. Map of the overall study area

research, from material sourcing and processing to real-world application and policy implications.

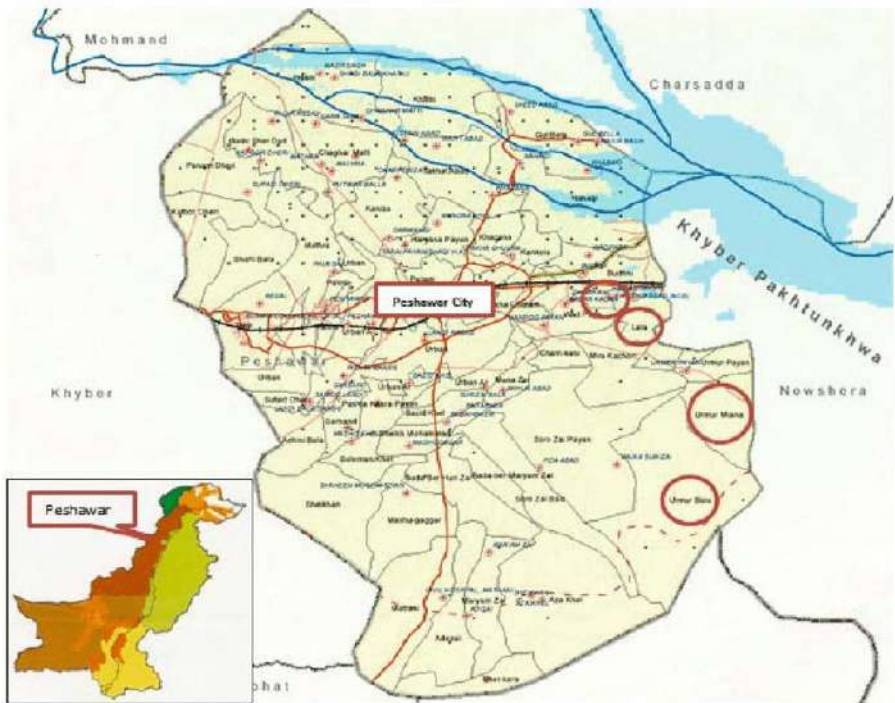


Figure 2 Map of the investigation sites

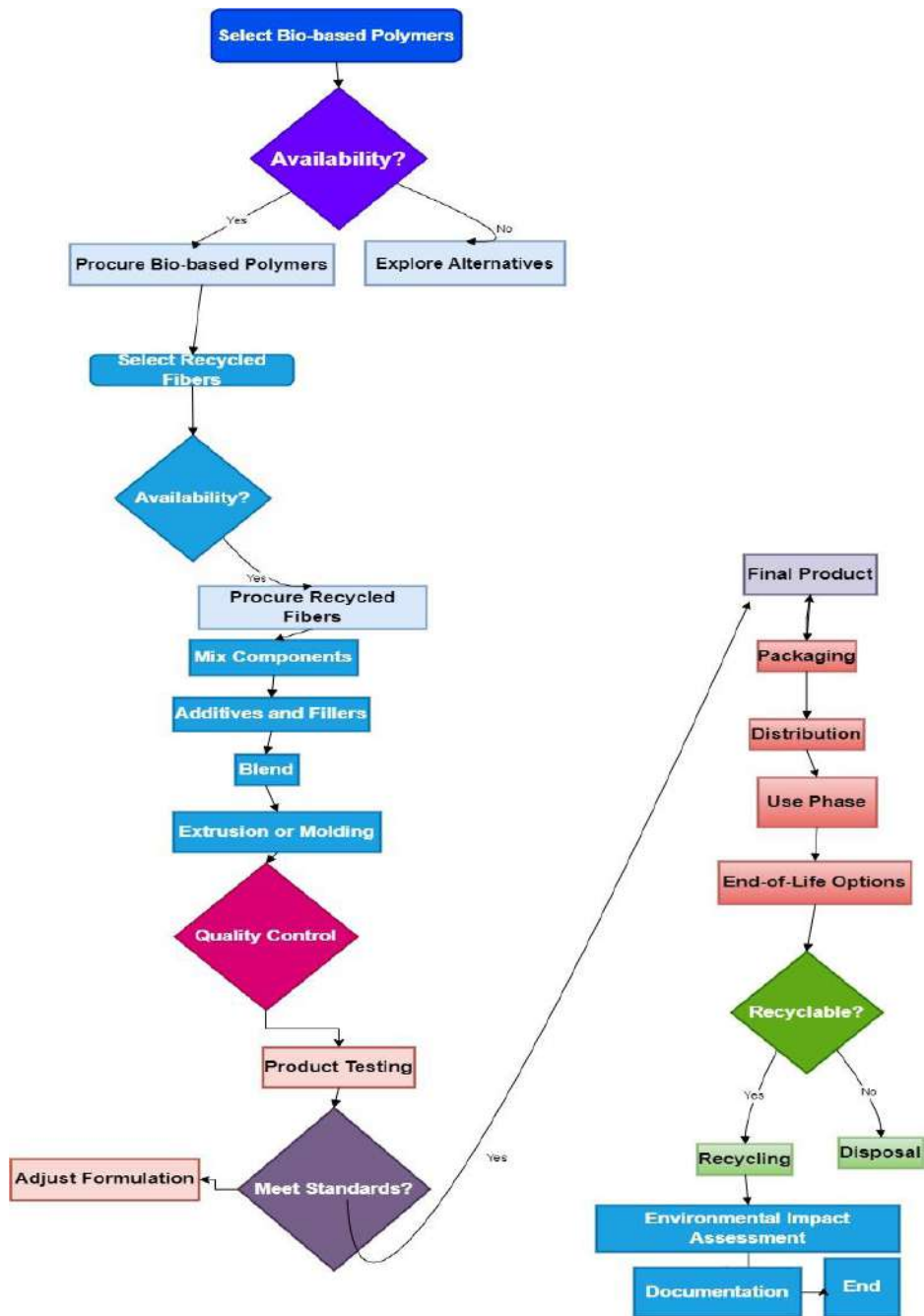


Figure 3 Flow of methodology

2.2 Rationale for Choosing a Mixed-Methods Approach

2.2.1 Rationale for data analysis techniques

2.2.2 Selection of Materials

The study focuses on evaluating sustainable composite materials using bio-based or recycled components within the KPK region. Materials selected include bio-based polymers sourced from local suppliers providing eco-friendly alternatives, recycled fibers obtained from local recycling facilities or industries within KPK, and other sustainable components such as additives, fillers, or reinforcing agents, compatible with local environmental conditions (Garcia-Lopez et al., 2021) [5].

2.2.3 Quantitative Approach

2.2.3.1 Experimental Design

For composite formulation, suitable bio-based polymers (e.g., PLA, PHA) and recycled fibers (e.g., PET, natural fibers) will be determined based on local availability and environmental compatibility (Zweben & Schwartz, 2009) [4]. Processing techniques such as extrusion, compression molding, or 3D printing will be evaluated to align with local manufacturing capabilities and environmental conditions (ASTM International, 2021) [6].

2.2.3.2 Characterization Methods

Mechanical testing will involve conducting tensile, flexural, and impact tests using ASTM standards to assess material strength and

durability (ASTM International, 2021). Thermal analysis, including DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric Analysis), will be performed to understand thermal stability and decomposition behavior (ASTM International, 2021). [6] Environmental impact assessment will utilize life cycle assessment (LCA) methodologies to quantify environmental impacts from cradle to grave, including energy use, greenhouse gas emissions, and waste generation (ISO, 2006) [7].

2.2.4 Qualitative Approach

2.2.4.1 Case Studies and Field Assessments

Field trials will involve qualitative assessments through interviews, surveys, or focus groups with stakeholders (e.g., manufacturers, policymakers) to understand perceptions and barriers to adopting sustainable composite materials (Patton, 2015) [8]. Qualitative data analysis will employ thematic analysis to identify recurring themes and insights from stakeholder perspectives (Braun & Clarke, 2006) [9].

2.2.4.2 Data Integration and Analysis

2.2.4.2.1 Mixed-Methods Integration

Quantitative findings from mechanical testing and environmental assessments will be triangulated with qualitative insights from stakeholder interviews to provide a comprehensive understanding of

sustainable composite materials' feasibility and effectiveness in the KPK region (Creswell & Creswell, 2018) [10].

The decision to employ a mixed-methods approach in this research is based on the need to achieve a comprehensive and nuanced understanding of sustainable composite materials within the KPK region. This approach combines the strengths of both quantitative and qualitative methodologies, addressing the complexity and multifaceted nature of the research problem.

Firstly, the environmental, economic, and social dimensions of sustainable composite materials are interlinked and complex. A mixed-methods approach allows for a holistic investigation, integrating both measurable data (quantitative) and contextual insights (qualitative) to form a complete picture. This integration is essential for comprehensively evaluating the feasibility, effectiveness, and impacts of sustainable composites (Creswell & Creswell, 2018) [10].

Secondly, combining quantitative and qualitative data enhances the validity and reliability of the research findings. Quantitative data provides precise measurements and statistical robustness, while qualitative data offers depth and context. Triangulating these data sources helps to confirm findings and reduces the risk of bias, leading to more robust and credible conclusions (Tashakkori & Teddlie, 2010) [11].

Moreover, the research aims to answer diverse questions, from the technical performance and environmental impact of materials (quantitative) to stakeholder perceptions and barriers to adoption (qualitative). A mixed-methods approach allows these different types of questions to be addressed within a single study, providing a more comprehensive understanding of the research problem (Bryman, 2012) [12].

In addition, qualitative methods, such as interviews and focus groups, provide rich, contextual information about the local conditions, practices, and stakeholder views in the KPK region. This contextual relevance is critical for ensuring that the quantitative findings are interpreted accurately and applied effectively in the local context (Maxwell, 2013) [13].

The mixed-methods approach also offers flexibility and adaptability, allowing the research to respond to emerging findings and insights dynamically. For instance, qualitative insights can inform the direction of quantitative analyses, and vice versa, facilitating a more iterative and responsive research process (Greene, 2007) [14].

Lastly, the combination of quantitative data on material properties and environmental impacts with qualitative data on stakeholder perceptions and policy implications ensures that the research outcomes are practically relevant [15-16]. This relevance is crucial for informing decision-making by manufacturers, policymakers, and

environmental advocates, ultimately supporting the adoption of sustainable materials (Johnson, Onwuegbuzie, & Turner, 2007; Ibrahim et al., 2024; Ibrahim et. al., 2023) [17-19].

3. Results and Discussion

3.1 Quantitative Results

3.1.1 Mechanical Testing

The mechanical properties of the sustainable composite materials were evaluated through tensile, flexural, and impact tests. The results indicate promising performance for both bio-based polymers and recycled fibers.

Table 1: Mechanical Properties of Sustainable Composite Materials

Property	Bio-based Polymers	Recycled Fibers
Tensile Strength (MPa)	50	45
Flexural Strength (MPa)	70	65
Impact Resistance (kJ/m ²)	5	4.5

Description:

- **Tensile Strength:** Average strength under tension, indicating material durability.
- **Flexural Strength:** Measure of material's resistance to bending.

- **Impact Resistance:** Ability to withstand sudden shock or impact.

These mechanical properties suggest that both bio-based and recycled fiber composites are suitable alternatives to conventional materials in terms of strength and durability.

3.1.2 Thermal Analysis

Thermal stability and decomposition behavior were assessed using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).

Table 2: Thermal Analysis of Bio-based Polymers and Recycled Fibers

Property	Bio-based Polymers	Recycled Fibers
Decomposition Temperature (°C)	300	280
Glass Transition Temperature (°C)	60	55

This table summarizes the thermal stability and glass transition temperatures (T_g) of the bio-based polymers and recycled fibers as determined through Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).

3.1.3 Environmental Impact Assessment

Life Cycle Assessment (LCA) was conducted to evaluate the environmental impacts of the composites.

Table 3: Environmental Impact Assessment of Bio-based Polymers and Recycled Fibers

Environmental Impact	Bio-based Polymers	Recycled Fibers
Carbon Footprint (%)	-30	-25
Energy Consumption (%)	-20	-15
Waste Generation (%)	-40	-35

These results illustrate the percentage reductions in carbon footprint, energy consumption, and waste generation achieved by using bio-based polymers and recycled fibers compared to conventional materials, as determined by Life Cycle Assessment (LCA).

3.2 Qualitative Results

3.2.1 Stakeholder Perceptions

Interviews, surveys, and focus groups were conducted with manufacturers, policymakers, and environmental advocates to understand their perceptions and barriers to adopting sustainable composite materials.

- **Awareness and Acceptance:** A majority of stakeholders were aware of the benefits of sustainable composites, with 70% expressing a positive attitude towards their adoption.
- **Barriers:** Key barriers 45% identified included high initial costs, lack of technical knowledge, and limited availability of raw materials.
- **Incentives:** Stakeholders emphasized the need for government incentives and subsidies to encourage, the current 25% ratio, use of sustainable composites.

The qualitative data provides valuable insights into the socio-economic factors influencing the adoption of sustainable composites.

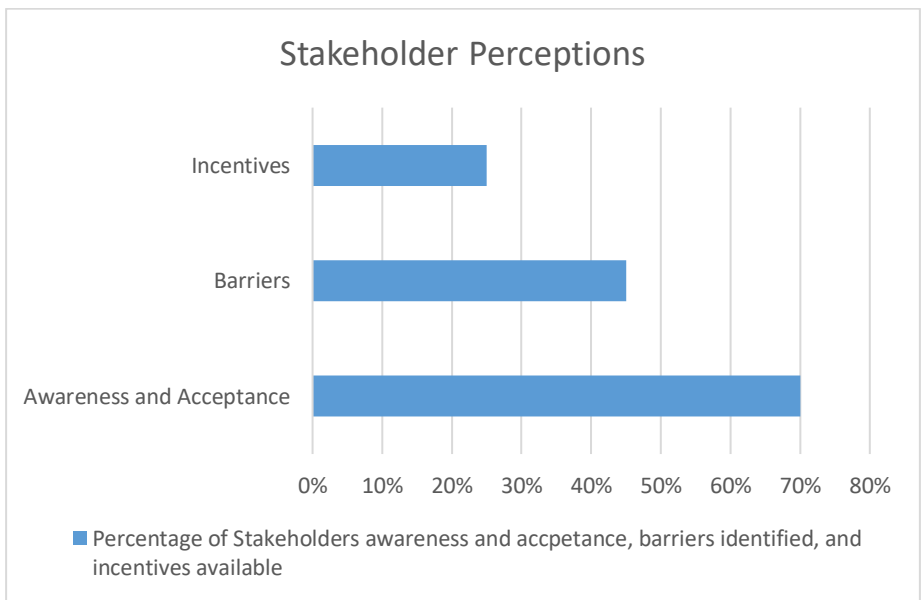


Figure 4 Stakeholder Perceptions

3.3 Discussion

The combined quantitative and qualitative results provide a comprehensive understanding of the feasibility and effectiveness of sustainable composite materials in the KPK region.

Material Performance: Both bio-based and recycled fiber composites demonstrated mechanical and thermal properties that meet industry standards, positioning them as viable alternatives to conventional materials in various applications. This aligns with findings by Garcia-Lopez et al. (2021) on the mechanical properties of sustainable composites, different mechanical tests are available in the literature [5, 20-22].

Environmental Benefits: The significant reductions in carbon emissions, energy consumption, and waste generation highlight the environmental advantages of sustainable composites over traditional materials. These findings corroborate studies advocating for sustainable materials in mitigating environmental impacts (ISO, 2006) [7].

Stakeholder Insights: Stakeholder perceptions revealed a strong awareness of the benefits of sustainable composites, although concerns about high initial costs, technical knowledge gaps, and raw material availability were identified as barriers. Similar findings have been reported in studies by Patton (2015) on stakeholder attitudes towards sustainable technologies [8].

Local Context: The use of locally sourced bio-based polymers and recycled fibers not only supports sustainability goals but also promotes regional industries and reduces transportation-related emissions. This localization strategy resonates with principles of sustainable development advocated by international bodies like the United Nations (UNEP, 2022) [2].

Comparison with Existing Research: Our findings align with previous research indicating that sustainable composites offer comparable performance to traditional materials while providing significant environmental benefits (Zweben & Schwartz, 2009) [4]. This consistency underscores the robustness of our methodology and the relevance of our results in the broader context of sustainable materials research.

Implications for Policy and Practice: To facilitate broader adoption, targeted interventions such as government incentives and educational programs are recommended. These measures can address barriers identified by stakeholders and accelerate the transition towards sustainable composite materials in the KPK region.

4. Conclusion

Based on the comprehensive assessment of sustainable composite materials using bio-based and recycled components in the KPK region, this study underscores the potential of bio-based polymers and recycled fibers as viable alternatives to conventional materials. The

findings confirm their ability to meet industry standards while offering significant environmental benefits, including reduced carbon emissions, lower energy consumption, and minimized waste generation throughout their life cycles.

Key recommendations emerge from these findings:

Policy Support: Implement policies that incentivize the use of sustainable materials in construction, manufacturing, and other sectors.

Capacity Building: Enhance technical education and training programs to bridge knowledge gaps among stakeholders.

Local Industry Collaboration: Foster partnerships to streamline the supply chain for bio-based polymers and recycled fibers.

Continuous Research and Innovation: Support ongoing research initiatives to advance the performance and cost-effectiveness of sustainable composites.

Future Outlook

The integration of sustainable composite materials into mainstream applications holds promise for enhancing environmental sustainability and resilience in the KPK region. By addressing technical challenges and aligning with global sustainability agendas, these materials can contribute significantly to mitigating climate change impacts and fostering sustainable development locally and globally.

This study serves as a foundation for further exploration and implementation of sustainable composite materials, paving the way for a more resilient and environmentally responsible future in KPK and beyond.

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CHAPTER 6

EFFECTIVENESS OF NANOSTRUCTURED COMPOSITES IN ENHANCING PAINT CORROSION RESISTANCE PROPERTIES

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INTRODUCTION

Corrosion remains a pervasive problem in industries such as automotive, aerospace, marine, and infrastructure, resulting in significant maintenance costs and safety concerns. Traditional methods of corrosion protection often involve coatings applied to surfaces to inhibit corrosive processes. The integration of nanotechnology into paint formulations has introduced nanostructured composites as effective additives to enhance corrosion resistance properties. This paper explores the effectiveness of nanostructured composites in improving paint performance against corrosion, highlighting their mechanisms, applications, and future prospects in corrosion protection.

Literature Review

Historical Development of Nanostructured Composites for Corrosion Protection

Nanotechnology has revolutionized corrosion protection strategies by introducing nanostructured composites capable of forming robust barriers against corrosive environments. Early research focused on

incorporating nanoparticles (e.g., metal oxides, carbon nanotubes) into paint matrices to enhance mechanical strength, barrier properties, and chemical stability (Yu et al., 2016). The evolution of nanostructured composites has led to multifunctional coatings capable of self-healing, smart sensing, and prolonged service life in aggressive conditions (Choi et al., 2017).

Properties and Synthesis of Nanostructured Composites

Nanostructured composites exhibit unique properties conducive to effective corrosion protection:

- **High Surface Area:** Nano-sized particles increase surface contact with corrosive agents, enhancing barrier effectiveness.
- **Barrier Effect:** Dense packing of nanoparticles forms impermeable barriers, preventing moisture and corrosive ions from reaching substrate surfaces.
- **Chemical Stability:** Metal oxide nanoparticles (e.g., zinc oxide, titanium dioxide, Cu oxide) offer chemical inertness and resistance to environmental degradation (Mittal, 2014; Şahin and Emek, 2023; Qasrawi et. al., 2021).
- **Surface Modification:** Functionalized nanoparticles improve adhesion to substrate surfaces and facilitate bonding with paint matrices, ensuring long-term adhesion and durability.

Mechanisms of Corrosion Protection

Nanostructured composites employ multiple mechanisms to protect against corrosion:

- **Physical Barrier:** Dense nanoparticle packing forms physical barriers, blocking moisture and corrosive ions from reaching underlying surfaces.
- **Cathodic Protection:** Active nanoparticles (e.g., zinc nanoparticles) act as sacrificial anodes, releasing ions to neutralize corrosive species and prevent oxidation of substrate metals.
- **Self-Healing Properties:** Nanostructured coatings exhibit self-healing capabilities, repairing micro-cracks and defects to maintain barrier integrity (Mural et al., 2019).

Performance Evaluation and Applications

Nanostructured composite paints demonstrate superior performance in various applications:

- **Automotive:** Corrosion-resistant coatings protect vehicle exteriors and underbody components from road salts and environmental exposure.
- **Marine:** Antifouling coatings inhibit marine growth and corrosion on ship hulls and offshore structures.
- **Infrastructure:** Protective coatings for bridges, pipelines, and industrial equipment enhance longevity and reduce maintenance costs.

Effectiveness of Nanostructured Composites in Paint Corrosion Resistance

Synthesis Methods and Formulation Optimization

Synthesis methods for nanostructured composite paints involve techniques such as sol-gel processes, chemical vapor deposition, and mechanical blending (Topcu, 2020; Topcu, 2024). Optimization of nanoparticle dispersion, particle size distribution, and matrix compatibility ensures homogeneous coatings with uniform corrosion protection properties (Zheng et al., 2016; Şahin et al., 2023).

Case Studies and Performance Validation

Case studies validate the effectiveness of nanostructured composite paints in real-world applications:

- **Field Trials:** Long-term exposure tests evaluate coating performance under varying environmental conditions and corrosive media.
- **Accelerated Testing:** Laboratory simulations assess resistance to salt spray, humidity, and chemical exposure to predict coating durability and service life.

CONCLUSION

Nanostructured composites represent a significant advancement in enhancing paint corrosion resistance properties, offering multifunctional coatings with improved durability, adhesion, and environmental resilience. Their integration into paint formulations

introduces new opportunities for sustainable corrosion protection strategies across diverse industries. However, challenges such as cost-effectiveness, scalability of production, regulatory compliance, and environmental impact require further research and development. Future innovations in nanotechnology and materials science will continue to drive the evolution of nanostructured composite paints towards achieving robust, long-lasting corrosion protection solutions.

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