THEORETICAL AND APPLIED PERSPECTIVES IN NATURAL SCIENCES AND MATHEMATICS

DOĞA BİLİMLERİ VE MATEMATİKTE TEORİK VE UYGULAMALI PERSPEKTİFLER

Editör: Doç. Dr. Gülşah SAYDAN KANBEROĞLU

DUVAR

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İÇİNDEKİLER

Chapter 1

Analysis of the Algol Type Eclipsing Binary Star V910 Mon Using Tess Data

Özlem EKİNCİ[1][2], Burcu ÖZKARDEŞ[3]

1. Introduction

Systems consisting of at least two components connected by gravitational forces and moving around a common center of mass according to Kepler's laws are defined as Binary Stars. The most important parameter determining the evolution process of a star is the stellar mass. For this reason, determining the masses of stars allows us to obtain important information about their evolutionary processes. In fact, a star's mass can only be determined if it is a member of a binary system. Therefore, binary stars are one of the most important celestial bodies in astrophysics because they allow the calculation of basic parameters such as temperature, radius, luminocity, etc., in addition to the mass.

The first information about the change of 2 mag. in the brightness of the star β Persei, which is the prototype of Algol-type systems, and the repetition of this change with a period of approximately 3 days was given by Goodricke (1783). According to the Roche model given by Kopal (1959), such systems belong to the class of detached or semi-detached. The star β Persei (i.e. Algol) is a semi-detached system, and these type stars are called as the classical Algol. The second

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components of classical Algols have filled their Roche lobes. There is a mass transfer towards the primary component, and the secondary one is in a further phase in the evolutionary state. This phenomena, which is contrary to the general acceptance in terms of the evolutionary status of binary stars, is known as the Algol Paradox (Crawford, 1955). Here, the massive component first evolves and reaches its own maximum size, and the mass then decreases as a result of the rapid mass transfer. Thus, the mass of the companion that gives the matter increases. In the detached Algols, both components are inside their own Roche lobes; therefore, the distance between their centers of mass is large. Hence, it is thought that they do not affect each other in the evolutionary process.

A detailed study including Algol type systems was made by İbanoğlu et al. (2006). In this study, 74 detached (DBs) and 61 semi-detached (SDBs) close binary systems were considered and the average mass ratio values were found to be 0.88 for DBs, 0.27 for SDBs, 0.30 for SDBs with periods less than 5 days and 0.22 for SDBs with periods greater than 5 days. In the same study, the luminosities of DBs and SDBs were plotted according to the orbital period and effective temperature (i.e., HR diagram), respectively. Accordingly, the luminosities of DBs tend to increase as the orbital periods of DBs increase. According to their positions in the HR diagram, the components of DBs are unevolved stars and remain within the main sequence band. The luminosities of both components of SDBs increase parallel to the orbital period. All primary components of SDBs are located within the main sequence band, while all secondary components evolved from the main sequence.

There are numerous studies for period analysis of Algol type systems in the literature. Accordingly, not only mass transfer/loss mechanisms but also the other mechanisms such as possible third body gravitationally connected to the system, magnetic activity and apsidal motion are discussed (Değirmenci et al. (2003); Erdem et al. (2007); Erdem et al. (2011); Yılmaz et al. (2017); Pop et al. (2017)).

In this study, we aimed to photometrically investigate the eclipsing binary star V910 Mon classified as an Algol type system, which is in the field of the TESS satellite. In the literature, V910 Mon, which is one of the less studied systems, is one of the NSVS (Northern Sky Variability Survey) variable star sources, and is classified as an EA-type star with the spectral type AOV (Otero et al. 2004). Qian et al. (2018) determined the spectral type, effective temperature, log g and metallicity ([Fe/H]) parameter of approximately 3196 EA-type binary stars with LAMOST spectral data, and gave these parameters for V910 Mon to be G0, 6010 K, 4.12 and -0.12, respectively. There is no detailed study on the analysis of the system. Basic parameters of V910 Mon from the SIMBAD database is given in Table 1.

Table 1. Equatorial coordinates (α, δ), BV magnitudes and GAIA parallax of V910 Mon.

α	δ	B (mag.)	V (mag.)	π_{GAIA} (mas)	Ref.
$06^h\ 40^m\ 13.7^s$	$+04^\circ\ 09'\ 40.1''$	11.56	11.06	2.8514	SIMBAD[4]

2. Tess Data

The photometric data of V910 Mon are provided by the observations by the TESS[5] (Transiting Exoplanet Survey Satellite) satellite. The main objective of this satellite, which is to search for exoplanets by transit method, is to observe about 200,000 stars in the neighborhood of the Sun. The TESS detector makes broadband observations in the wavelength range of 600 - 1000 nm, the central wavelength of which corresponds to the classical Cousins I band (IC = 786.5 nm). The spectral response curve of the detector is given in Figure 1.

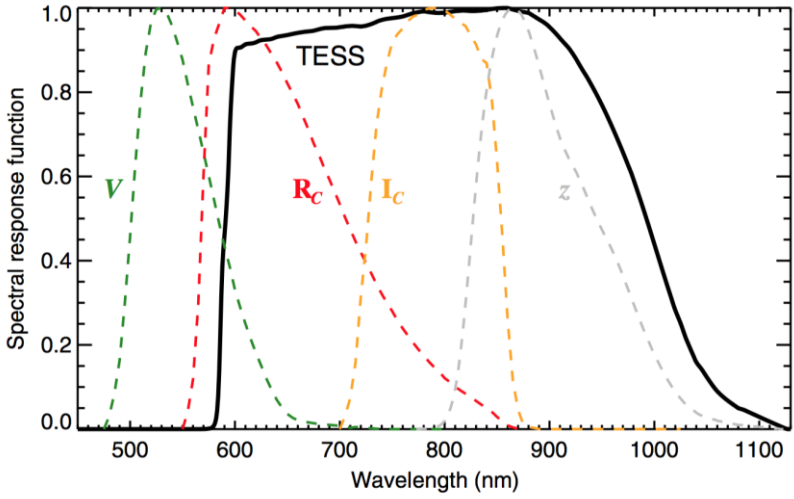

Figure 1. Spectral response function of the TESS detector (black line).

V910 Mon was observed by the TESS satellite at long cadance with exposure times 1800 s and 600 s. These observations were recorded in sectors 6 and 33,

[4] https://simbad.u-strasbg.fr/simbad/sim-fid
[5] https://exoplanets.nasa.gov/tess/

respectively. TESS data can be downloaded from the MAST[6] (the Mikulski Archive for Space Telescopes) archive. Here, the "SAP (Simple Aperture Photometry) Flux" values corresponding to "QUALITY = 0" were taken into account. All instrumental brightnesses were converted to normalized flux (see Figure 4).

3. Minimum Light Times

The period variation of an eclipsing binary star can be studied by O-C diagram analysis, which is generated via minimum light times. In this study, published data were taken from the O-C Gateway database[7] . In addition, new minimum light times were obtained from the TESS light curves of the system using Minima (vers.27) software given by B. Nelson[8]. The eclipsing times are given in Table 2.

Table 2. Eclipsing times of V910 Mon. The values in parentheses are the error values according to the last digit.

BJD (+2400000)	Min. Type	Reference	BJD (+2400000)	Min. Type	Reference
52714.5090	I	O-C Gateway	59203.9345(5)	I	TESS sector 33 (this study)
57074.2678	I		59306.8881(7)	I	
57799.4128	II		59209.8421(8)	I	
58542.2893	I		59212.7962(5)	I	
58471.4000(7)	I	TESS sector 6 (this study)	59215.7496(8)	I	
58474.3536(5)	I		59218.7039(7)	I	
58480.2614(1)	I		59221.6574(10)	I	
58483.2150(9)	I		59224.6108(9)	I	
58486.1701(2)	I		59202.4583(10)	II	TESS sector 33 (this study)
58469.9235(5)	II	TESS sector 6 (this study)	59205.4114(6)	II	
58472.8774(5)	II		59208.3654(8)	II	
58475.8310(6)	II		59211.3191(7)	II	
58481.7384(5)	II		59217.2265(8)	II	
58484.6922(7)	II				

[6] https://mast.stsci.edu/portal/Mashup/Clients/Mast/Portal.html
[7] https://var.astro.cz/en/Stars/16623
[8] https://www.variablestarssouth.org/resources/bob-nelsons-software-tools/software-by-bob-nelson

4. Analysis

4.1. New Light Elements

By combining all the minimum light times obtained from the TESS light curves of V910 Mon with the published ones, the O-C values of the system were calculated, and the O-C diagram was created according to the epoch number. When the diagram is examined, a linear variation is seen (see Figure 2). Therefore, a linear regression fit was applied to all O-C values. Hence, the correction values of the light elements, T0 and P, were found, and new light elements were determined, which is given in the equation (1). The O-C diagram of V910 Mon and the residuals are given in Figure 2.

$$\text{Min I (BJD\_TDB)} = 2459224.6107(\pm 0.0003) + \text{Ex}2.95376721(\pm 0.0053) \quad (1)$$

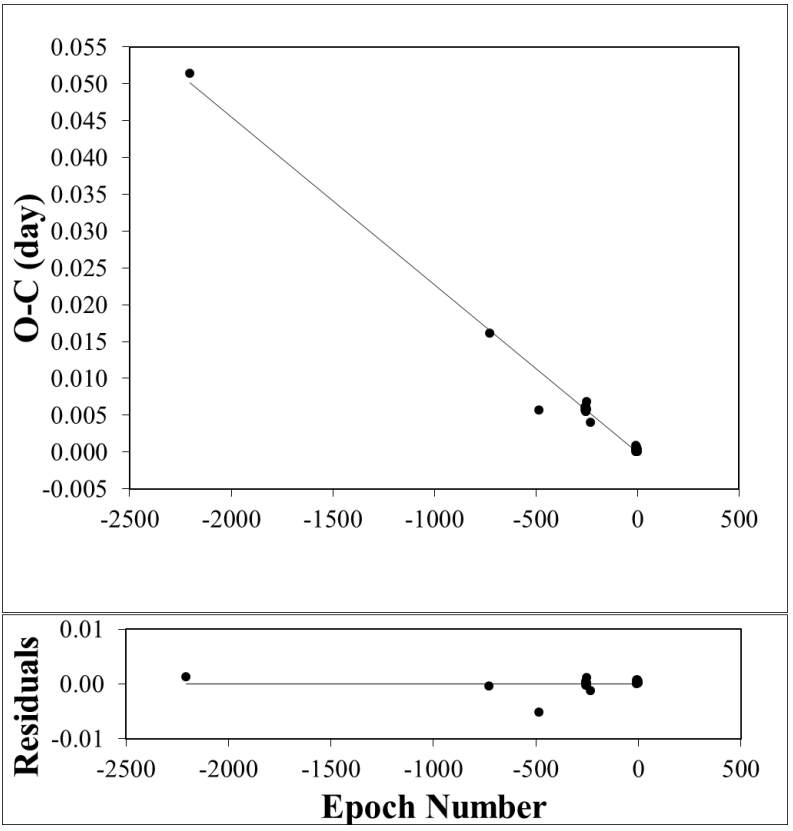

Figure 2. Top: O-C diagram for V910 Mon. Lower panel: Residuals from the best linear fit.

4.2. Light Curve Modeling

The basis of the light curve analysis method is to calculate the light curve parameters of a binary star that exhibits brightness variation by fitting a theoretical curve generated by the parameter values entered by the user to the observational data. The parameter remaining from the sum of the differences between the observed and calculated light curves is R ($R = \Sigma(O_i - C_i)^2$). The smaller value of the residual sum of squares R, the better the fit of the data.

In this study, the widely used Wilson-Devinney (WD) method (Wilson and Devinney, 1971) was applied to TESS light curve from sector 33. Initial parameters are needed to perform mathematical calculations in the light curve solution. In other words, we need to take some parameters as constants in the input file. These parameters are; primary component's temperature (T_1), albedo coefficients (A_{12}), gravitational darkening exponents (g_{12}), limb darkening coefficients ($X_{1,2}$,$Y_{1,2}$) and mass ratio (q). Accordingly, the parameter values taken as constants during the analysis are as follows: The temperature of the primary component is fixed at 6811 K given by Qian et al. (2018). The values of the limb darkening constants were determined from the tables given by Claret and Bloemen (2011) and Claret et al. (2013) according to the square-root limb darkening law. The bolometric gravitational darkening exponents of the components were taken as 0.32 for the convective envelope (T<7200 K) according to the study of Lucy (1967). The bolometric reflections of the components were taken as constant at 0.5 for convective atmospheres, according to the study of Rucinski (1969). It's been accepted that the component stars are co-rotating. It was assumed that the orbit of the system is circular. The unspot model was applied to the light curve due to the lack of O'Connell effect.

If the mass ratio q, which is one of the program parameters, is not determined by the spectroscopic data, mass ratio scanning (q-search) is performed for determinig the input value of q. There is no spectroscopic observations of V910 Mon in the literature. Therefore, q-scan was performed (see Figure 3). Here, scanning was performed with 0.1 increments for the range of 0.1-1.5. The mass ratio value that minimizes $\Sigma(O_i - C_i)^2$ was determined as 0.8.

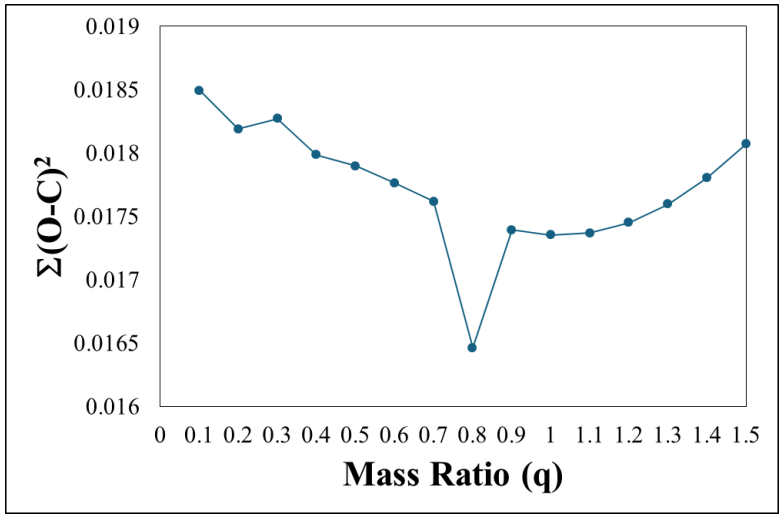

Figure 3: q-search for V910 Mon.

The free parameters in the WD analysis are orbital inclination, phase shift, mass ratio, temperature of the second component, luminosity of the primary and secondary components and third light. The solution results are given in Table 3. The comparison of the observational and theoretical curves is given in Figure 4.

Table 3. *Results of WD analysis for V910 Mon*.

Parameter	**Value**	**Parameter**	**Value**
i (°)	88.9 (±0.7)	Ω_2	9.4669(±0.0286)
Phase shift	0.0003 (±0.0002)	$l_1/(l_1+l_2+l_3)$ *(TESS)*	0.59 (±0.01)
T_1 (K)	6010 (fixed)	l_3 *(%)*	7 (±1)
T_2 (K)	5875 (±26)	r_1 (mean)	0.14(±0.01)
$q = M_1/M_2$	0.8695 (±0.0212)	r_2 (mean)	0.10(±0.01)
Ω_1	7.8468 (±0.0152)	Σ(O-C)^2 *(TESS)*	0.0359

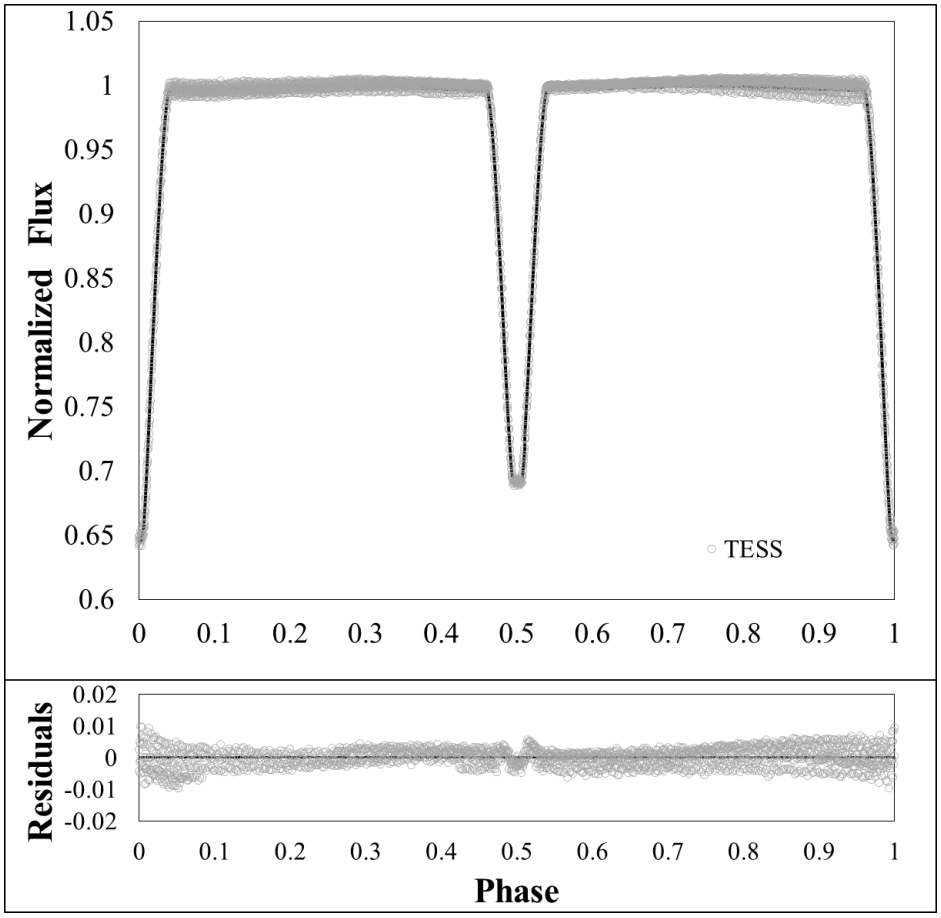

Figure 4. Comparison of TESS and theoretical light curves of V910 Mon (top) and residuals (bottom).

5. Results And Discussion

According to the light curve analysis' results of V910 Mon, the binay star is a detached binary with the primary and secondary component filling the Roche lobes by 47% and 40%, respectively. The Roche surface geometry of the system in 2D (Bradstreet (2005)) is shown in Figure 5.

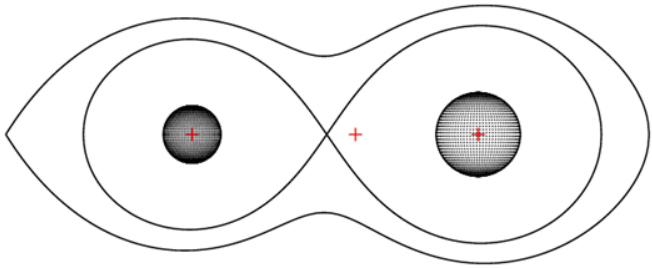

Figure 5. Surface geometry in 2D for V910 Mon.

Since there is no spectroscopic study of the eclipsing binary, the absolute parameters of the component stars have been estimated. While the mass of each component were defined using Kepler's third equation and the mass ratio from the photometric solution, while their luminosities were calculated using the Stefan-Boltzmann law. In the calculations, the Sun values (T_{eff} = 5771.8±0.7 K, $M_{bo}l$ = 4^m.7554±0.0004 and g = 27423.2±7.9 cm/s^2) given by Pecaut and Mamajek (2013) were taken into account. The bolometric corrections (BC) of the components of the system were determined from Flower (1996) according to their surface temperatures. The absolute parameters and errors of the system are given in Table 4. The distance of V910 Mon was determined using the distance module, which takes into account the interstellar absorption. The distance of V910 Mon is in agreement within the error limits when compared to the distance according to the parallax of GAIA DR3 (Gaia Collaboration, 2022).

In order to examine the evolutionary status of the system, the positions of the component stars are plotted on the Teff - L/Lsun diagram (i.e. Hertzprung-Russell (HR) diagram) in a logarithmic scale, together with the detached binary stars taken from Southworth (2015). According to the HR diagram (Figure 6), both components are located within the zero-age main sequence (ZAMS) band. It is also seen that the components of the system are compatible with the archival detached binary components. The age of the system was tried to determine using the isochrones given by Girardi et al. (2000) for solar abundance. Accordingly, the best representative age of the components was found to be 5.624 Gyr.

Table 4. *Estimated absolute parameters of V910 Mon.*

Parameter	Value	
	Primary comp.	Secondary comp.
a ($R_\odot$)	10.79 ± 0.94	
M ($M_\odot$)	1.04 ± 0.03	0.90 ± 0.05
R ($R_\odot$)	1.55 ± 0.14	1.12 ± 0.10
L ($L_\odot$)	2.82 ± 1.07	1.35 ± 0.52
M_V (mag.)	3.15 ± 0.41	
log g (cgs)	4.07 ± 0.12	4.29 ± 0.05
d (pc)	367 ± 69	
d_{Gaia} (pc)	350.7 ± 1.9	

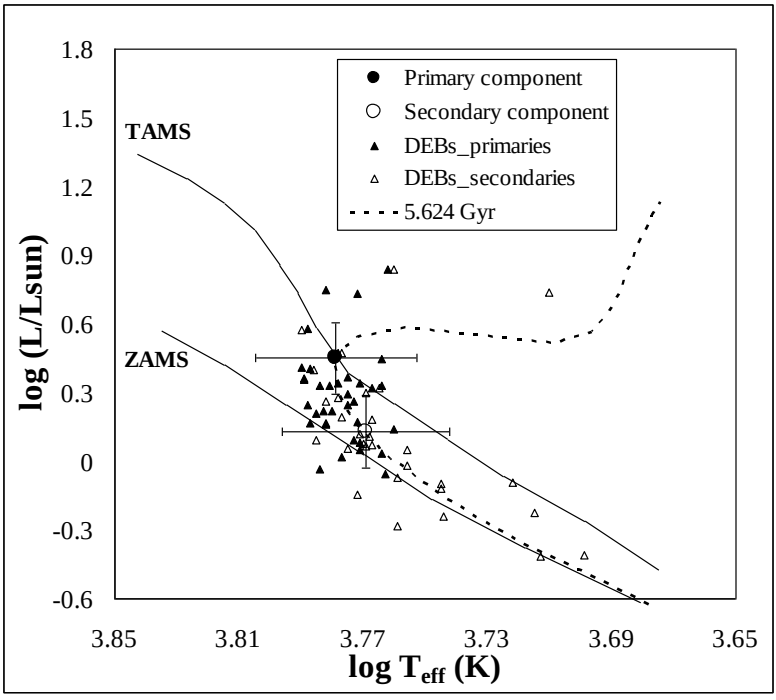

Figure 6. Positions of the components of V910 Mon on the HR diagram. ZAMS and TAMS are shown in the diagram with solid lines according to solar abundance (Z = 0.019) from Girardi et al. (2000).

Spectroscopic and multi-colour photometric observations are needed to accurately determine the absolute parameters of V910 Mon. In this study, the light curve analysis revealed a third light contribution of 7%. More eclipsing times are required for detailed analysis of the existence of the third component.

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Chapter 2

Biological Activities of Lichen Secondary Metabolites

Şeyda Nur KALIN[1]

1. Introduction

Natural products of plant origin have been used as a traditional therapeutic modality in many civilizations for more than five thousand years (1). Even today, plant materials, as a valuable source of therapeutic agents, continue to play an important role in the treatment of various diseases such as cardiovascular diseases, infectious diseases, cancer chemotherapy, and disorders of lipid metabolism (2–5). Today, the challenges associated with natural products are drug discovery based on natural products with promising activities, difficulties in isolation of active principles, technical barriers to screening natural products in high-throughput assays against molecular targets (4). Due to these difficulties, scientists have had to turn their attention to other organisms.

Many studies have shown that lichens, a natural product of a mutualistic relationship between fungi and cyanobacteria or fungi and algae, are productive organisms for the synthesis of a wide variety of secondary metabolites (1). Lichens have the ability to survive in harsh living conditions thanks to the secondary metabolites they produce. Lichens have been used since ancient times for perfumes, food, dyes, traditional medicine, and various ethnic purposes (6). Lichens have the potential to produce unique secondary metabolites with different physicochemical and biological activities (7). Lichen secondary metabolites, of which there are more than a thousand varieties, include many classes of compounds, including aliphatic acids, amino acid derivatives, sugar alcohols, macrolytic lactones, monocyclic aromatic compounds, chromones, quinines, depsides, xanthones, terpenoids, depsidones, depsones, dibenzofurans, steroids, diphenyl ethers and carotenoids (8). The

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production of specific secondary metabolites requires appropriate culture conditions such as added sugars, nutrient media, polyols, light, temperature, pH, and stres (9). Lichen secondary metabolites have unique biological properties such as antimicrobial, immunomodulatory, antihepatotoxic, antidiabetic, antioxidant, antiviral, and anticancer (10–12). Therefore, many studies on lichen secondary metabolites have been the focus of many researchers (10,13,14).

Therefore, elucidation and understanding of the utilization of lichens and their products may be important for the future use of lichens as a natural medicine. This review focuses on the biological activities of various lichen species and in particular their potential use in cancer therapies.

2. Lichens

Lichens are defined as compound organisms that contain algae (e.g., Trentepohlia or Trebouxia) or cyanobacteria (Nostoc) and live between filaments of more than one fungal species in a mutualistic relationship (6,15). The estimated number of lichen species ranges from 13.500 to 30.000, with the expectation of an increase as research in this field continues to expand (16). Lichens are mainly classified according to their growth form, habitat, internal structure, and fungal partners (Figure 1).

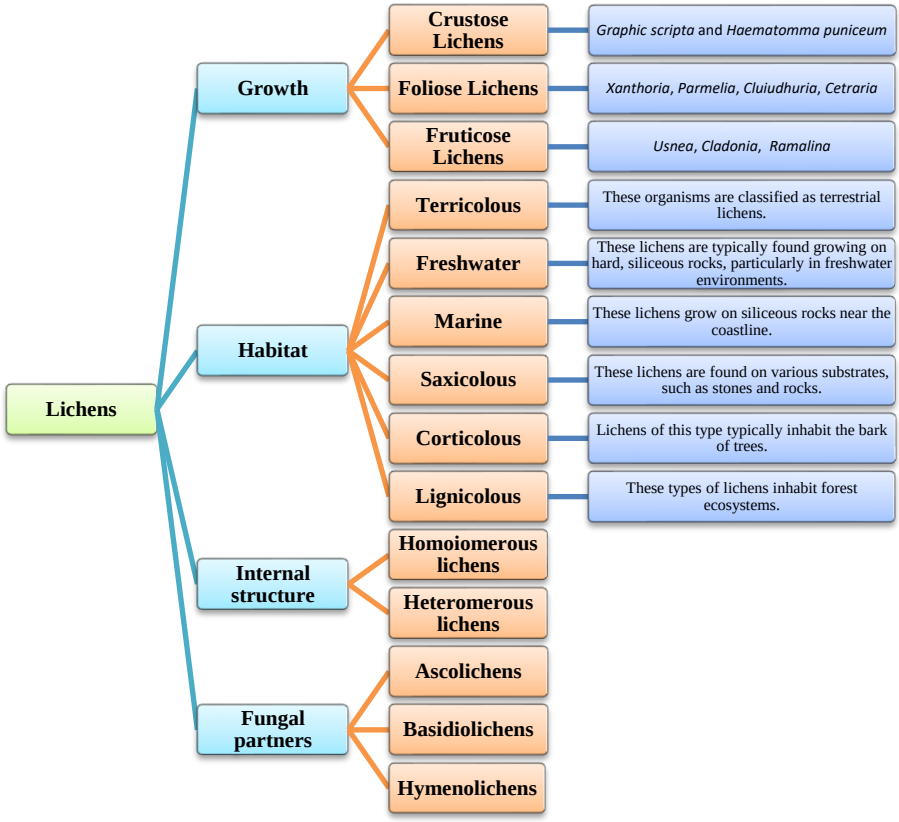


Figure 1. Classification of lichen types

Lichens are important components of primary producers in a wide variety of substrates and habitats, including some of the most extreme conditions on Earth (desert, south and north pole, etc.). Thus they can also survive in extreme environmental conditions. The resilience of lichens is mainly due to their slow metabolism, their capacity to survive for months in a state of metabolic rest, and their production of many specialized bioactive molecules that provide them with chemical protection.

According to their chemical structure, lichens produce a large number of bioactive substances, including many classes of compounds such as quinones, lactones, depsidones, depsons, dibenzofurans, phenolic compounds (17).

Figure 2. Images of several different lichen species (18).

3. Biological activities of lichens

Lichen secondary metabolites produced by lichens are chemical compounds with industrial, nutraceutical, and therapeutic values (19). Lichens involve several biosynthetic pathways to produce various compounds, mainly the acetyl polymalony, shikimic acid, and mevalonic acid pathways (Figure 3) (20). Most of the secondary metabolites of lichen are produced via the acetyl-polymalonyl pathway and chemical compound classes such as chromone, xanthone, emodin, depside, dibenzofuran, anthraquinone, depsidones, androcrocin are synthesized via the acetyl-polymalonyl pathway. Examples of this group include atranorin, barbatic acid, diffractic acid, squamatic acid, evernic acid, divaric acid, norstictic acid, lobaric acid, salazinic acid, usnic acid, and emodin. Compounds originating from the shikimic acid synthesis pathway include terpenylquinone and pulvinic acid derivatives. The secondary metabolites of lichen are synthesised via the mevalonic acid pathway, which also produces terpenes, steroids, and carotenoids. Ergosterol, ursolic acid, and zeorin are notable examples of such molecules (17).

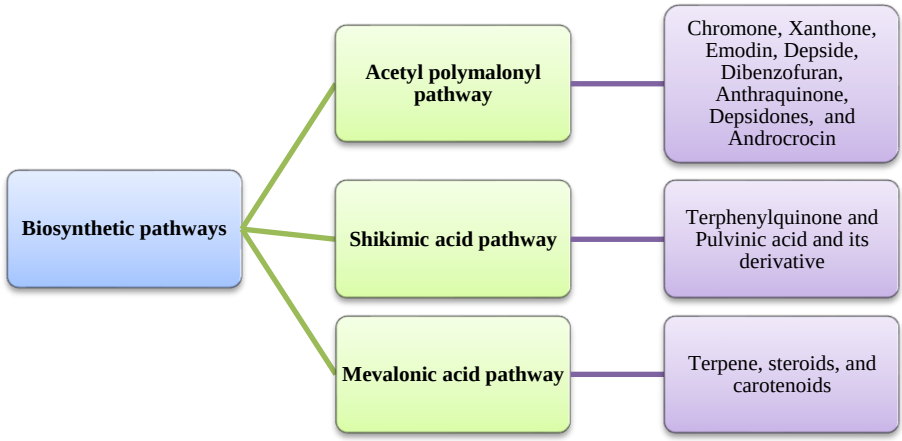


Figure 3. Biosynthetic pathways involved in the synthesis of lichen metabolites

The active compounds of lichens isolated by methods such as thin layer chromatography (TLC) or high performance liquid chromatography (HPLC) have many biological properties (21,22). Scientists have identified lichen metabolites as a research topic due to their unique properties (Table 1).

Lichen secondary metabolites exhibit antifungal activity against some pathogenic fungi, such as *Candida albicans*, *Microsporum gypseum*, *Trichophyton rubrum*, and *Trichophyton mentagrophytes*. In the literature, *Xanthoria parietina*, *Caloplaca cerina*, *Protousnea poeppigii*, *Cladonia convoluta*, and *Usnea florida* lichens have been reported to have antifungal activity (23–25).

Some lichens show antiviral properties and can be used as potential sources of pharmaceutically useful chemicals. For example, usnic acid extracted from *Ramalina celastri* showed specific antiviral activity against *Tacaribe* and *Arenaviridae* virus (26). It has also been reported that *Ramalina farinacea* can be used as an antiviral agent against DNA and RNA viruses (7).

Lichens are known to have antibacterial activity, such as vulpinic acid, evernic acid and usnic acid found in the genera *Evernia*, *Cladonia*, *Usnea*, *Alectoria*, *Cetraria*, and *Ramalina* (17). Romangi and Dayan reported that usnic acid has an antibiotic effect against *Mycobacterium*, *Staphyllococcus*, and *Streptococcus* (27). Ingolfsdottir et al. reported that protolicesterinic acid isolated from *Cetraria islandica* had antibacterial properties against *Helicobacter pylori* bacteria (28).

Lichens are among the natural sources with strong antioxidant effects. Lichens provide protection against oxidative damage caused by the accumulation of free radicals, which have important functions in many chemical processes in cells, with the secondary compounds they produce. For example, extreme conditions such as

high UV-B, sunlight, winter darkness, low temperature, and drought lead to increased oxidative stress. It was reported that lecanoric acid from *Umbilicaria antarctica* was found to be the most effective antioxidant in superoxide anion and free radical scavenging (11). Lichens such as *Lobaria pulmonaria* and *Usnea longissima* exhibit strong antioxidant properties thanks to the abundance of phenolic compounds (29). Some of the lichen species such as *Umbilicaria cylindrica, Pseudoevernia furfuraceae, Flavoparmelia caperata, Parmelia pertusa, Parmelia sulcata, Evernia prunastri, Hypogymnia physodes, Nephroma parile, Anaptychya ciliaris, Parmelia centrifuga, Usnea florida, Usnea longissima,* and *Lobaria pulmonaria* were found to have antioxidant activities (30–33).

Table 1. Biological properties of lichen secondary metabolites.

Lichen species	**Natural compound**	**Activities**	**Ref.**
Parmotrema grayana	Erythrin	Antioxidant	(19)
Roccella montagnei *Pseudoevernia furfuracea* *Evernia prunastri* *E.divaricata*	Evernic acid	Antioxidant, antibiotics, cytotoxic, anticancer	(34–37)
Cetraria islandica *Hypotrachyna cirrhata* *Cornicularia aculeata*	Protolichesterinic acid	Anti-inflammatory, antimicrobial, antibacterial, proliferation, anticancer	(38,39)
Xanthoria parietina	Parietin	Cytotoxic,antimicrobial	(40)
Toninia candida, *Usnea strigose* *Stereocaulon montagneanum* *Ramalina farinacea*	Norstictic acid	Antioxidant, antimicrobial, cytotoxic	(41–43)
Parmotrema tinctorum *Umbilicaria antarctica* *Roccella montagnei*	Lecanoric acid	Antioxidant, anticancer, antifungal	(44–47)
Stereocaulon alpinum *S.paschale* *Usnea longissima* *Cladonia sp.* *Parmelia saxatilis*	Lobaric acid	Cytotoxic, antimicrobial, anti-inflammatory, antioxidant, enzyme inhibition	(48–54)
Cetrelia monachorum	Perlatolic acid	Anti-inflammatory	(55)
Usnea spp./Ramalina spp./U. longissima	Usnic acid and derivatives	Anticancer, antimicrobial, enzyme inhibitor, analgesic, antimutagenic activity,anti-inflammatory, antiallergies, antivirus	(34,56–58)
Platiamatia glauca	Caperatic acid	Anti-inflammatory, cytotoxity, Central nervous system therapeutics	(47,59)

Letharia columbiana *L.vulpina* *Pseudocyphellaria flacicans* *Vulpicida pinastri*	Vulpinic acid	Antibiotics, anticancer	(34,60)
Parmotrema austrosinense	Orsellinic acid	Antimicrobial	(61)
Usnea longissima	Barbatic acid	Anticancer	(62)
Usnea longissimi *Usnea subcavata* *Protousnea magellanica*	Diffractaic acid	Anti-inflammatory, antioxidant,antiviral, analgesic, gastroprotective, anticancer	(13,29,62–66)
Pseudevernia furfuracea	Olivetoric acid	Antimicrobial , antioxidant	(67,68)
Parmotrema austrosinens *Cladonia rangiferina* *Stereocaulon evolutum*	Atranorin and derivatives	Antimicrobial , anticancer, anti-hepatitis C virus	(34,47,61,69)

4. Anticancer effect of lichen secondary metabolites

Due to the dramatic increase in cancer incidence and mortality rates, new treatment methods have become important. In particular, the potential of natural ingredients with high effectiveness and fewer side effects in cancer treatments is being investigated. Lichen secondary metabolites exhibit anti-proliferative, cytotoxic, anti-migratory, anti-invasive, antioxidant, pro-apoptotic, anti-proliferative, and anti-tumourigenic properties (70–73).

Cytotoxic and anti-proliferative effects of lichen metabolites have been observed in different cancer types such as breast cancer, lung cancer, glioblastoma multiforme, prostate cancer, liver cancer, cervical cancer, pancreatic carcinoma, colon cancer (10,37,47,64,74–76). Lichen metabolites may exert cytostatic effects on cancer cells by arresting the cell cycle in G0/G1, G2/M, or S phases, and may also exert cytotoxic effects by triggering cell death mechanisms such as apoptosis, autophagy or necrosis (77). In one study, usnic acid suppressed proliferation by arresting the cell cycle (G0/G1 and G2/M) in human gastric carcinoma BGC823 and SGC7901 cell lines (78). Usnic acid was reported to suppress apoptosis in hepatocellular carcinoma SNU-449 and HepG2 cell lines, arresting the cell cycle at G0/G1 and G2/M checkpoints (77). Vulpinic acid exhibited a cytostatic effect by arresting the cell cycle in breast cancer MDA-MB-453 and MCF-7 cell lines (79). In another study, salazanic acid from *Parmotrema cetratu*m has shown anti-proliferative effects in colon cancer HT-29 cell line (80).

Lichen metabolites play a role as apoptosis inducers by regulating cell death mechanisms in cancer cells (81). That is, these metabolites can modulate mRNA levels of apoptosis-related products such as pro-/anti-apoptotic proteins of the Bcl-2 family, caspases, p38, p53 (70,82). Furthermore, they can induce

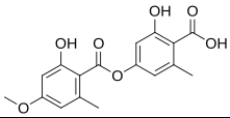
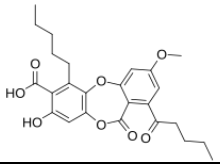
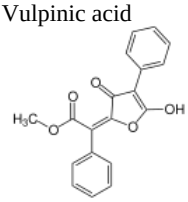
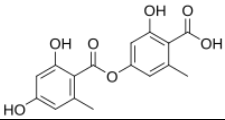
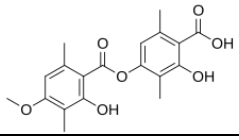
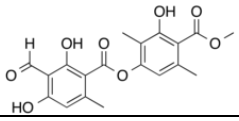
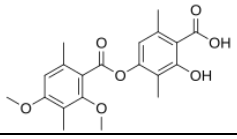
cell death through cleavage of poly (ADP-ribose) polymerase (PARP), a stress response protein that regulates chromatin structure and repairs damaged DNA, activation of c-Jun N-terminal kinase (JNK) signalling or inactivation of mammalian target of rapamycin (mTOR) (77,83). Lichen metabolites can modulate genes associated with cell cycle control (cyclin D1 and c-myc), apoptosis (BIRC5), cell migration (MMP7) or other regulators such as Axin2 by targeting the Wnt/β-catenin pathway (81,84). Moreover, these metabolites may exhibit anticancer effects through modulation of pathways by regulating STATs, PI3K/Akt/mTOR, and Paxillin/Rac-1 signalling cascades (42,84,85).

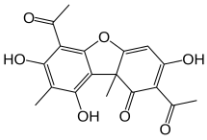
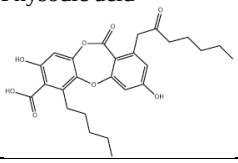
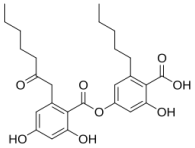
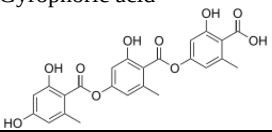
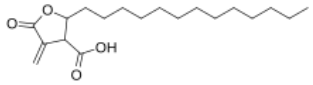
Lichen metabolites have the ability to suppress metastasis, one of the leading causes of cancer-related deaths. Thus, they can regulate the tumour microenvironment, metabolic processes, metastasis-related genes and important signalling pathways to prevent metastasis in cancer cells (47). Usnic acid isolated from the lichens *Usnea florida*, *Flavocetraria nivalis*, *Alectoria samentosa*, and *Alectoria ochroleuca* has shown significant inhibitory potential against invasion and migration in human lung cancer (A549, H1975, H1650, and H460 cell lines). Atranorin isolated from *Stereocaulon caespitosum* suppressed the migration and invasiveness of human hepatocellular carcinoma Huh-7 and SK-Hep1 cell lines (86). Ramalin, a metabolite isolated from *Ramalina terebrata*, suppressed wound healing, migration and invasion of HCT116 cells (87). Physciosporin isolated from *Pseudocyphellaria coriacea* inhibited the migration and invasion of human lung cancer H1650,A549, and H1975 cell lines through down-regulation of KITENIN-mediated AP-1 activity, Cdc42, N-cadherin, and Rac1 (88).

Phenolic compounds of lichens may show antioxidant effects by exhibiting high free radical scavenging ability. The protective effects of lichens against oxidative damage can be determined by observing oxidative stress markers. In the literature, *Dirinaria consimilis*, a tropical lichen, has been reported to show anticancer activity in human cervical carcinoma HeLa cells and human brain glioblastoma U-87 MG cells by promoting the increase of reactive oxygen species (ROS) and suppressing glutathione S-transferase (GST), catalase (CAT), and superoxide dismutase (SOD), antioxidant enzyme activities and glutathione (GSH) levels (89). Vulpinic acid, evernic acid, and diffractaic acid inhibited thioredoxin reductase 1 (TrxR1) enzyme activities, a member of the antioxidant enzyme system, in breast, cervical, lung, and liver cancer types (13,37,64,76,79,90).

Table 2 shows an overview of the anticancer effects of some lichen secondary metabolites.

Table 2. Secondary metabolites of lichens: sources and mechanisms of action.

Active Compound/ Chemical structure	**Cancer types**	**Activities**	**Ref.**
Evernic acid 	Glioblastoma carcinoma, breast cancer, lung cancer, cervical cancer	Decreased proliferation Suppressed migration Inhibition of antioxidant enzyme activity	(37,91–93)
Lobaric acid 	Cervical cancer, colon cancer	Decreased proliferation Induced cell cycle arrest Induced apoptosis	(83,94,95)
Vulpinic acid 	Malignant mesothelioma, vulvar carcinoma, keratinocyte cells carcinoma, rhabdomyosarcoma ,mouse fibrosarcoma, breast cancer, cervical cancer	Decreased proliferation Suppressed migration Induced apoptosis Inhibition of antioxidant enzyme activity	(64,79,96–98)
Lecanoric acid 	Larynx carcinoma	Decreased proliferation Induced cell cycle arrest Induced apoptosis	(99)
Barbatic acid 	Cervical cancer, lung cancer, breast cancer, prostate cancer	Decreased proliferation	(62)
Atranorin 	Prostate cancer, melanoma cancer	Decreased proliferation Suppressed invasion	(100)
Diffractaic acid 	Cervical cancer liver cancer, breast cancer, lung cancer,	Decreased proliferation Suppressed migration Induced apoptosis Inhibition of antioxidant enzyme activity	(13,64,76,90)
Usnic acid	Breast cancer, colon cancer, lung cancer leukemia cancer, prostate cancer, ovarian	Decreased proliferation Inhibition of angiogenesis, Inhibition of invasion and migration	(101–103)

	cancer,melanoma cancer	Induced cell cycle arrest Increased ROS levels Induced apoptosis	
Physodic acid 	Lung cancer, colon cancer	Cytotoxic effect Inhibition of invasion Induced apoptosis	(104,105)
Olivetoric acid 	Glioblastoma carcinoma	Cytotoxic effect	(106)
Gyrophoric acid 	Melanoma cancer	Cytotoxic effect	(107)
Protolichesterinic acid 	Cervical cancer, prostate cancer	Induced apoptosis Decreased proliferation	(108,109)

5. Conclusion

Lichen secondary metabolites, rich in bioactive compounds, are of great interest due to their applicability as therapeutic agents in the treatment of many diseases, including cancer. Despite the important effects of lichen metabolites, so far there are no relevant clinical studies in the literature that provide insight into their anticancer activity in humans. Facilitating the isolation and characterization of lichen metabolites with the help of modern equipment and methodologies and defining their complex biological cellular effects provide favorable conditions for accelerating future clinical testing and research involving the use of lichen-derived anticancer drugs in medical practice. Therefore, further studies are needed to determine the potential clinical uses of lichen metabolites and to clarify their beneficial effects in cancer patients or people at risk.

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Chapter 3

Quantum Dot Integration in Energy Storage Systems: Current Status, Future Directions, Opportunities and Challenges

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1. Introduction

Quantum dots (QDs), specifically carbon quantum dots (CQDs) and graphene quantum dots (GQDs), have become vital materials in energy storage systems such as supercapacitors and batteries. Their distinctive properties, such as a high surface area, outstanding electrical conductivity, and adjustable electrochemical characteristics, make them excellent candidates for improving the electrochemical performance of energy storage devices.

GQDs, a subclass of QDs, exhibit remarkable properties that enhance their effectiveness in energy storage applications. Their small size and high surface area facilitate better interaction with electrolytes, essential for the rapid charge-discharge cycles needed in supercapacitors (Ansari, 2022; Lee et al., 2016). Research indicates that GQDs can be integrated into composite materials, improving the overall electrochemical performance of devices. For instance, GQDs have been utilized to create nanocomposite films that demonstrate superior supercapacitor properties compared to traditional materials (Dinari et al., 2016).

QDs have garnered considerable attention due to their distinctive optical and electronic properties, making them highly advantageous across various applications. In energy storage, QDs enhance the performance of supercapacitors and lithium-ion batteries by improving charge transfer efficiency and the stability of electrodes. In the field of optoelectronics technologies, such as QLED TVs, due to their

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exceptional color purity and tunable emission wavelengths. Furthermore, QDs are essential in solar cells, enhancing light absorption and conversion efficiency. Their applications extend to biomedical imaging and biosensors, leveraging their fluorescence properties to enable high-resolution imaging and precise disease detection (Fig. 1) (Huang & Zhu, 2013; Reshma & Mohanan, 2019).

The application of QDs in energy storage systems primarily stems from their high degree of surface development, facilitating adequate charge storage and high current density during discharge processes. For example, CQDs have been shown to enhance the electrochemical performance of various electrodes, resulting in improved charge storage capabilities in supercapacitors and batteries (Breczko et al., 2024; Gao et al., 2024; Prasath et al., 2018). The incorporation of CQDs into electrode materials can significantly boost specific capacitance and energy density, as illustrated in studies where CQDs were utilized to modify nickel sulfide and manganese oxide composites, leading to supercapacitors with impressive performance metrics (Sahoo et al., 2018; Xia et al., 2015).

Quantum dots (QDs) can be synthesized from various sustainable precursors, including biomass. The synthesis methods affect their characteristics and properties. Hydrothermal synthesis is notable; for example, Xu et al. created highly photoluminescent carbon dots from nitrogen and sulfur co-doped precursors, and carbon quantum dots derived from aloe demonstrated effective fluorescence through a green process. This approach allows for precise particle size control and promotes biocompatibility, which is crucial for medical applications(Xu et al., 2015; Jia et al., 2022).

Another significant synthesis approach is microwave-assisted synthesis, which offers rapid processing times and high efficiency. Gupta and Nandi reported the synthesis of sulfur-doped carbon dots via microwave-assisted pyrolysis, achieving high quantum yield, thus demonstrating the technique's effectiveness in enhancing luminescent properties (Lin et al., 2019). This method reduces reaction times significantly compared to conventional thermal processes, allowing for quicker and potentially more cost-effective production of QDs.

Alternatively, the solvothermal synthesis method is widely recognized for its versatility and is used for various quantum dot compositions, particularly those involving metal chalcogenides such as CdSe and ZnS. The solvothermal approach allows for controlling size and composition by adjusting the temperature and solvent type. For example, $CuInS_2$ quantum dots were synthesized using a solvothermal technique, demonstrating their viability in photovoltaic applications as sensitizers for TiO_2 photoanodes (Peng et al., 2012). In addition, this method can enhance QDs' crystallinity, which is critical for their optical properties (Hoang et al., 2020). Successive Ionic Layer Adsorption and Reaction (SILAR) is another well-

documented method that has been effective for synthesizing core/shell quantum dots like CdSe/ZnS. This technique allows for precise control over the shell thickness, which can significantly affect the photoluminescent properties of the quantum dots. SILAR has been utilized to create high-quality CdS, CdSe, and their composites with polymers, facilitating their integration into electronic devices (Rahayu & Lee et al., 2024). This method can achieve excellent surface passivation, enhancing the QDs' stability and luminescence (Wang et al., 2024).

In contrast to traditional chemical methods, biological synthesis presents a novel approach by utilizing natural precursors for quantum dot fabrication. Studies have illustrated the feasibility of generating CQDs from biomass, such as rice husk or quinoa straw, which showcases the potential for sustainable and eco-friendly nanomaterial production (Wang et al., 2024; Ye et al., 2024). This approach reduces reliance on hazardous chemicals typically involved in the quantum dot synthesis process, contributing to the development of green nanotechnology.

Moreover, physical methods like laser ablation and electrochemical techniques have also been explored for quantum dot generation. For instance, laser ablation enables precise control over the quantum dot size through energy input and material type (Ye et al., 2024). Electrochemical synthesis provides advantages in terms of scalability and control of stoichiometry, though it may require sophisticated setups (Penner, 2000).

Regarding the surface modification of quantum dots, various ligand exchange and stabilization techniques have been developed to enhance their dispersibility and functionalization potential. For example, modifying CdSe QDs with polyethylene glycol (PEG) improves solubility in aqueous media and broadens their application scope (Wenger et al., 2017). Proper surface functionalization is crucial for ensuring the stability of QDs in biological environments and enhancing their interactions with biological systems (Tani et al., 2010).

The impact of size on quantum dots' optical properties is profound, primarily due to quantum confinement effects. Smaller quantum dots generally exhibit a blue shift in their absorption and emission spectra, while larger ones demonstrate redshifts, influencing their usability in applications requiring specific optical characteristics (Shakouri et al., 2019). This relationship emphasizes the importance of precise control over synthesis parameters to achieve desired properties.

To conclude, the synthesis methods for quantum dots are diverse, encompassing various chemical and physical techniques, which impart distinct properties critical for their application. Hydrothermal, microwave-assisted, and solvothermal methods are prominent due to their control over particle characteristics, while SILAR offers the specificity needed for core/shell structures. Biological and physical methods provide sustainable and precise alternatives, respectively. Ultimately, understanding

these synthesis methods paves the way for advancements in quantum dot applications across multiple sectors, including healthcare, electronics, and environmental science. Generating CQDs from waste materials promotes environmental sustainability and provides a cost-effective solution for energy storage applications (Wu et al., 2023; Singh & Gupta, 2024). This aspect is especially relevant as the demand for efficient and eco-friendly energy storage solutions continues to grow.

QDs, particularly CQDs and GQDs, are crucial in advancing energy storage technologies. Their unique properties enable significant improvements in the performance of supercapacitors and batteries, positioning them as a central focus of ongoing research and development in energy storage systems.

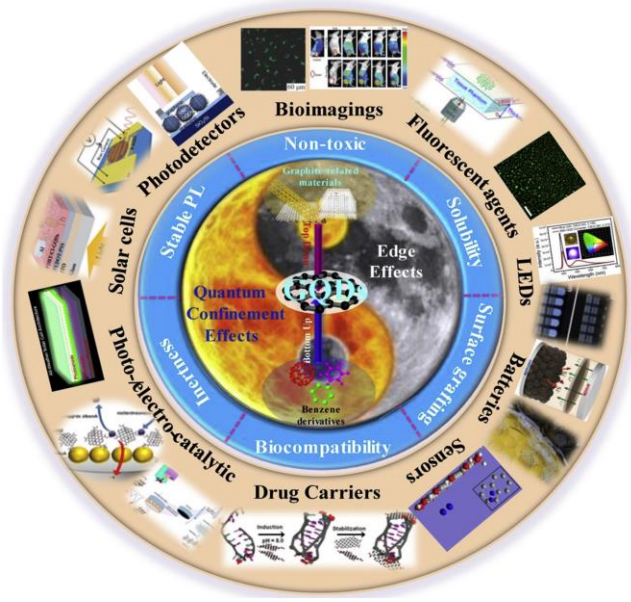

Figure 1. Properties and applications of graphene quantum dots (Tian et al., 2018). Reprinted with permission from Elsevier.

2. Fundamentals and Synthesis Methods of Quantum Dots

QDs offer broad absorption spectra, allowing a wide range of excitation wavelengths. This enables the simultaneous excitation of multiple colored QDs with a single wavelength. Additionally, their narrow light emission is advantageous for imaging since it reduces overlap between different dyes, overcoming a limitation of conventional broad-emission dyes. QDs can be easily tuned in terms of core size, composition, and surface coatings to emit light at precise wavelengths from ultraviolet (UV) to infrared (IR). Specifically, near-infrared (NIR) luminescent QDs

possess excellent optical properties, with NIR light (700–1000 nm) providing minimal background interference and deep tissue penetration, making them ideal for bio-imaging applications, electronics and photovoltaics (Kargozar et al., 2020). Their diverse synthesis techniques cover various methodologies that affect their physical and chemical properties. This chapter delves into several predominant methods of synthesizing QDs, including top-down and bottom-up approaches, colloidal and hydrothermal synthesis, and utilizing biological materials (Fig. 2).

Figure 2. Synthesis methods of quantum dots (Liu et al., 2021). Reproduced with permission from Wiley, Copyright 2021.

The top-down approach mainly involves reducing more extensive materials into QDs. Microfluidic systems have attracted significant attention due to their capability to provide precise control over synthesis parameters, resulting in uniform particle sizes. For instance, microfluidics enable the careful manipulation of the reaction environment, fostering a more controlled nucleation and growth process. This ultimately leads to QDs with enhanced properties compared to traditional methods (Nightingale & Mello, 2010). Furthermore, the synthesis of semiconductor QDs through laser ablation has been highlighted in the literature. In this technique, particles are generated from vaporized material, which is rapidly cooled to facilitate quick nucleation and growth (Kim et al., 2017).

The bottom-up approach encompasses methods in which atoms or molecules are combined to form QDs. A key technique within this framework is colloidal

synthesis, which allows researchers to tailor the optical properties of QDs by controlling essential variables such as precursor concentration and reaction time. Pospisilova et al.. (2016) demonstrated the scalability of zinc oxide (ZnO) QD synthesis using colloidal methods, achieving high fluorescence quantum yields through careful process optimization. Furthermore, colloidal synthesis is often enhanced by applying organic or ligand coatings to prevent agglomeration, thereby improving stability for biomedical applications (Wagner et al., 2019).

Hydrothermal synthesis has emerged as an effective and eco-friendly method for producing carbon QDs (C-dots), utilizing naturally abundant materials and resulting in minimal hazardous byproducts. For instance, Kumar et al. (2016) employed Bovine Serum Albumin (BSA) in their hydrothermal process to create nitrogen-doped C-dots, achieving high fluorescence quantum yields. Similarly, Zhou et al. (2012) demonstrated that using agricultural waste, such as watermelon peels, for C-dot fabrication led to an environmentally sustainable synthesis process with desirable optical properties. One well-established method involves utilizing organic precursors, such as citric acid and ethylenediamine, to produce high-quality nitrogen-doped carbon quantum dots (N-CQDs) with photoluminescence quantum yields (PLQY) reaching as high as 80.6% through straightforward hydrothermal reactions (Wu et al., 2019). For example, Pei et al. emphasized that CQDs derived from biomass via hydrothermal carbonization are effective fluorescent probes for sensing applications due to their exceptional biocompatibility and sustainability (Pei et al., 2021). Continuous hydrothermal flow synthesis represents another effective method for producing QDs. This approach is energy-efficient and time-saving and guarantees the reproducibility and uniformity of the resulting QDs (Bărăgău et al., 2020). Kellici et al. successfully demonstrated the rapid synthesis of graphene QDs using this continuous flow technique, showcasing its versatility in generating various quantum nanoparticles from two-dimensional materials (Kellici et al., 2018). Integrating various doping elements can notably enhance the optical properties of QDs. For instance, in the study where hydrothermal methods were preferred, adding nitrogen and boron to CQDs improved their electronic structure and increased fluorescence stability (Jiang et al., 2019). The hydrothermal approach is particularly appreciated for its capacity to control nanoscale properties by adjusting different synthesis parameters, resulting in enhanced luminescence (Li et al., 2021). The hydrothermal synthesis of QDs offers significant advantages for producing environmentally friendly, highly luminescent nanomaterials. As featured in various studies, these materials are suitable for bioimaging, environmental sensing, and energy storage devices (Jia et al., 2022). Research conducted in recent years increasingly emphasizes the diverse sources of precursor materials and the

importance of optimizing synthetic routes to meet the specific requirements of emerging technologies (Li et al., 2021; Sahoo et al., 2018).

Biomass-mediated synthesis is becoming a promising, eco-friendly alternative for producing QDs. This technique utilizes plant extracts to facilitate the reduction and stabilization of metal ions, ultimately forming QDs. It leverages the inherent reducing and stabilizing properties found in various plant constituents. For instance, Tak et al. (2020) highlighted the potential of employing flower extract from Clitoria ternatea to synthesize GQDs, indicating a therapeutic application for Alzheimer's disease. This method provides an environmentally sustainable pathway for synthesizing QDs while integrating biological functionalities, making them well-suited for diverse biomedical applications. CQDs have been derived from date palm midrib and microcrystalline cellulose, demonstrating this approach's versatility and ecological benefits (Hassan et al., 2024; Wu et al., 2017). Wang et al. illustrated that biomass can be converted into carbon nanomaterials, emphasizing its sustainable nature and potential for commercial applications in sensor technology, mainly due to the low-cost characteristics of these materials (Wang et al., 2024). Moreover, a notable advantage of biomass-derived CQDs is their outstanding photoluminescence properties, rendering them ideal candidates for biosensing and bioimaging applications (Baker & Baker, 2010; Başkaya & Çeşme, 2021). The synthesis of cadmium sulfide (CdS) QDs using biomass exemplifies the effectiveness of this approach. Research has indicated that plant extracts and fungal mycelium can reduce and stabilize agents in producing luminescent CdS QDs. For instance, Borovaya et al. (2014) demonstrated the successful application of plant hairy root cultures for generating CdS QDs, thereby establishing a foundational understanding of how natural enzymes contribute to QD formation. Similarly, Shivaji et al. (2019) found that waste tea leaves act effectively as biosurfactants in synthesizing CdS QDs, further noting the cytotoxic effects of these nanoparticles on cancer cells and highlighting their potential applications in biomedicine.

Recent studies underscore the increasing significance of nitrogen doping in enhancing the optical properties of biomass-derived QDs. N-CQDs exhibit impressive photoluminescence that can be finely tuned for specific applications, thereby boosting their utility across various fields, such as sensor technology and bioimaging (Fig. 3) (Başkaya & Çeşme, 2021; Wareing et al., 2021). Moreover, integrating environmentally sustainable practices into the synthesis process facilitates the development of QDs that meet performance criteria and help mitigate the environmental impacts associated with traditional synthesis methods (Thangaraj et al., 2019; Zhu et al., 2020).

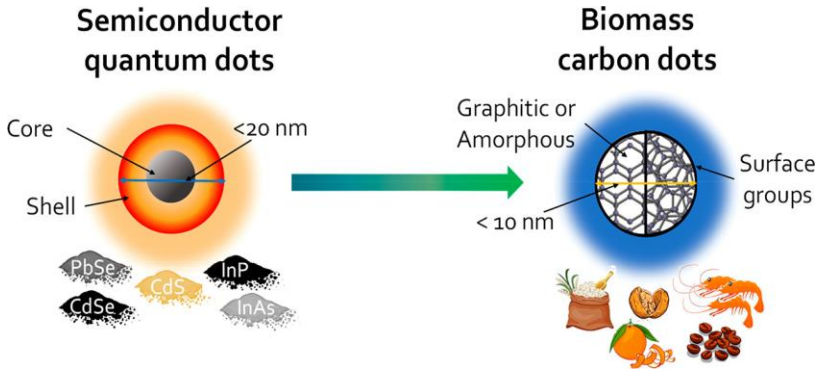

Figure 3. Differences between semiconductor QDs and biomass carbon dots (Wareing et al., 2021). Reprinted with permission from the American Chemical Society.

Microwave-assisted synthesis is an advanced technique that considerably shortens reaction times without compromising the quality of synthesized QDs. This method facilitates rapid heating, effectively enhancing nucleation rates and forming smaller and monodisperse QDs (Zhao et al., 2024). It has been successfully employed to produce CQDs with specific optical properties essential for sensing applications (İlter et al., 2023). One notable advantage of microwave-assisted synthesis is its capacity to generate high quantum yield (QY) carbon dots briefly. Research has demonstrated that this technique can efficiently synthesize blue-green emissive carbon dots with QY exceeding 25%. However, studies on synthesizing yellow and red emissive variants using similar methods remain limited (Ergüder et al., 2022).

Furthermore, Hagiwara and Horikoshi have shown that CQDs can be synthesized to achieve impressive luminescence, with a QY of 61% at 580 nm, under low-pressure microwave solvothermal conditions. This underscores the versatility of this method in producing a diverse range of photonic outputs (Hagiwara & Horikoshi, 2019). The microwave approach not only applies to carbon dots but also to metal-based QDs. For instance, Ren et al. (2021) demonstrated a one-step microwave synthesis of water-soluble silver sulfide QDs, which exhibited strong fluorescence and proved effective in bioimaging applications. Similarly, methods for cadmium-based QDs have been explored by Xuan et al. (2013). They introduced a one-pot microwave technique for the large-scale production of CdS nanocrystals, detailing how the synthesis conditions could be easily adjusted to customize the optical properties of the resulting QDs. In addition, employing microwave synthesis to produce alloyed QDs offers significant advantages, particularly in generating high-quality structures with tunable properties. Yang et al. (2012) highlighted synthesizing quaternary alloyed CdSeTeS QDs using microwave techniques,

demonstrating practical applications in biological imaging and advanced optoelectronic devices.

Wang et al. (2007) noted that thiol-terminated cadmium telluride QDs can be produced in aqueous solutions with significantly lower toxicity than traditional methods. This novel approach has paved the way for safer applications of QDs in biological settings, primarily due to effective encapsulation that reduces the risk of harmful substances leaching out.

The significance of chemical precursors in influencing the properties of QDs cannot be overstated. Liu et al. indicated that varying carbon sources can have a considerable effect on the photoluminescent properties of carbon dots, illustrating that careful selection of precursor materials can optimize specific quantum efficiencies and stability (Liu et al., 2016). Additionally, changes in the chemical environment—affected by different ligands—can further alter QD properties, thereby enhancing the tunability of their optical emissions (Lee et al., 2013).

Notably, the synthesis of QDs involves critical adjustment periods during the process. Solution aging can result in significant changes to optical properties due to restructuring at the nanoscale. This indicates the dynamic nature of QD synthesis, where both the initial conditions and subsequent treatment phases can profoundly influence the final result.

Moreover, innovative strategies are emerging, such as the encapsulation of QDs within silica matrices to enhance their stability and functionality across various applications (Nikdoost et al., 2017). These techniques effectively combine the optical advantages of QDs with silica's mechanical and thermal robustness, paving the way for advancements in photonic applications and beyond.

Another significant approach in QD synthesis is the creation of core-shell structures, which improve photoluminescent properties while minimizing toxicity. Shuklov et al. investigated the synthesis of telluride QDs, revealing that the core-shell configuration enhances stability and functionality (Shuklov et al., 2020). This dual-structured design allows for greater control over exciton behavior, thereby boosting the overall efficiency of QDs in optoelectronic devices.

In summary, the synthesis of QDs encompasses various methodologies, each offering distinct advantages and challenges. From traditional top-down and bottom-up approaches to innovative microwave and biomass-mediated techniques, the ability to carefully adjust synthesis parameters to align with photophysical properties sets the stage for customized nanomaterials. Ongoing exploration and refinement of these methodologies promise to unlock new applications within nanotechnology, particularly in areas such as biomedicine, environmental monitoring, and optoelectronics.

3. Applications of Quantum Dots in Energy Storage Systems

With the growing demand for efficient and sustainable energy storage solutions, researchers continually explore advanced materials to enhance performance. QDs have emerged as pivotal in advancing energy storage systems, particularly supercapacitors and batteries. Their exceptional properties—including high surface area, tunable electrical characteristics, and quantum confinement effects—have significantly improved electrochemical performance. Recent advancements in QD-based nanocomposites and novel synthesis methodologies have expanded their applicability in energy storage technologies (Fig. 4).

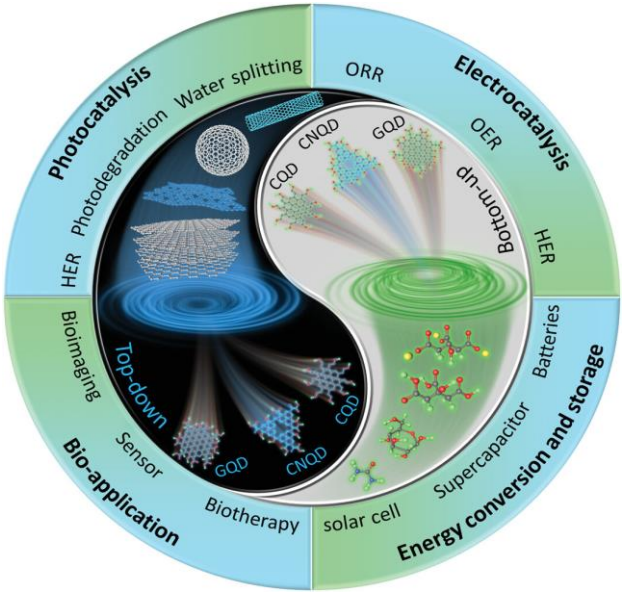

Figure 4. Application fields of QDs (Guan et al., 2023). Reproduced with permission from Wiley, Copyright 2023.

3.1. Quantum Dots in Batteries

Due to their unique electrochemical properties, QDs have emerged as promising materials in battery technologies. Their application in various types of batteries, such as lithium-ion, sodium-ion, and lithium-sulfur batteries, has garnered considerable research attention. The advantages provided by QDs include enhanced electrical conductivity, increased surface area, and efficacy in catalyzing electrochemical reactions. These properties can improve battery performance metrics such as capacity, cycling stability, and charge-discharge efficiency. The multifaceted application of QDs in battery technologies illustrates their critical role in advancing energy storage systems. Continuous research is warranted to optimize integration

processes and investigate novel QD materials that can lead to next-generation batteries with enhanced performance, longevity, and sustainability. As energy demands heighten globally, insights from ongoing QD studies will shape the future of portable and grid-scale energy storage innovations.

Recent studies have reported significant improvements in energy densities due to incorporating QDs in battery electrodes. The work by Lakshmi-Narayana et al. indicated that asymmetric supercapacitors using $NiCo_2O_4$/graphene QDs achieved an energy density of 69.5 $Whkg^{-1}$ and a power density of 2.2 $kWkg^{-1}$, demonstrating the potential of QDs to enhance performance metrics significantly (Lakshmi-Narayana et al., 2024). Such values emphasize the important role of QDs in advancing batteries capable of delivering high energy and power densities, which is critical in applications requiring rapid charging and sustained energy output.

QDs also enable improvements in the rate performance of electrodes, contributing to superior cycling stability and reversible capacities. Studies conducted by Qin et al. pointed out the properties of nitrogen-doped carbon-coated $NiS_{1.97}$ QDs, demonstrating that these QDs can enhance electron transport and interfacial utilization in magnesium-ion batteries. This highlights their critical role in achieving high performance under operational stresses (Fig. 5) (Qin et al., 2023).

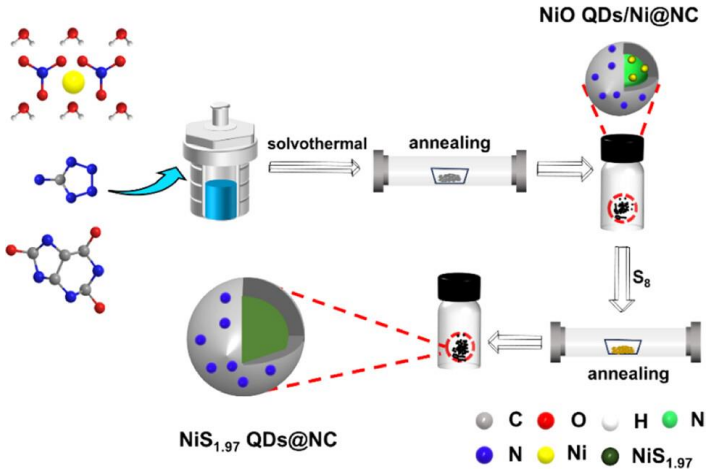

Figure 5. Schematic diagram of the synthesis of $NiS_{1.97}$ QDs@NC (Qin et al., 2023). Reprinted with permission from the American Chemical Society.

Another important aspect relates to the structural advantages QDs provide to electrodes. In the investigation by Deng et al., the integration of $ZnMn_2O_4$ QDs into carbon frameworks led to substantial improvements in the performance of aqueous zinc-ion batteries. This approach addressed issues like the Jahn–Teller effect, which often compromises cycling stability. It demonstrated the capacity for sustained

energy release, further highlighting the versatility of QDs across different battery chemistries (Deng et al., 2022).

QDs extend their application beyond traditional lithium and sodium systems. For instance, in lithium-sulfur (Li-S) batteries, functionalized QDs have shown exceptional catalytic effects, enabling efficient sulfur utilization while mitigating the shuttling effect of polysulfides. A study by Xu et al. (2018) indicated that incorporating black phosphorus QDs in porous carbon/sulfur cathodes led to high energy efficiencies with minimal capacity fade over prolonged cycles, achieving a capacity fading rate of only 0.027% per cycle after 1000 cycles. This emphasizes the essential function of QDs in promoting chemical reactions necessary for improved battery performance.

As QD technologies evolve, practical aspects of incorporating these materials into electrodes must be addressed. A research review by Xu et al. (2022) outlined several achievements and potentials of QDs in energy storage, bridging technological gaps such as material degradation and energy efficiency. Similarly, studies incorporating CQDs into sodium-ion batteries have reported significant advancements in capacity and cycling stability, illustrating the diverse applicability and growing interest in QDs as key materials for next-generation energy storage solutions (Shan-li et al., 2024).

The differences observed among various battery types demonstrate the significant effectiveness of quantum dots, firmly establishing their vital role in optimizing electrochemical reactions. For example, the study of Ma et al. with Mo_2N QDs and N-doped graphene nanosheets documented significant advances in interfacial electron transfer rates, supporting the development of high-capacity anodes structured for dendrite-free lithium-sulfur battery applications (Ma et al., 2022). This innovation indicates the potential for QDs to transition from ancillary materials to cornerstone components in battery architecture.

Comparative assessments of QD-infused batteries have revealed that sodium-ion batteries (SIBs) enhanced with CQDs achieved notable improvements in electrical conductivity and energy storage metrics (Thangaraj et al., 2023). The integration of QDs assists in achieving a balance between energy efficiency and quick discharge rates, which is critical for the dynamic consumption patterns of modern devices.

Applying QDs in batteries signifies a robust avenue for improving power and energy densities, opening pathways to next-generation energy storage systems with flexible applications, from consumer electronics to electric vehicles. Continuous exploration of their unique properties, interface optimization, and functional integration is crucial for leveraging their full potential within the rapidly evolving landscape of energy technologies.

3.1.1. Lithium-Ion Batteries (LIBs)

Incorporating QDs in lithium-ion batteries presents a significant advancement in enhancing their electrochemical performance, particularly in capacity and cycle life. QDs, with their unique nanoscale properties, facilitate improved charge transfer, accommodate structural changes during cycling, and serve as effective hosts for active materials, thereby contributing to superior battery performance.

A simple template-assisted method was employed to synthesize SnO_2 QDs dispersed on conducting polypyrrole (PPy) sheets. The SnO_2 QDs@PPy anode exhibited impressive lithium storage capabilities, achieving a capacity of 1252 $mAhg^{-1}$ at a discharge rate of 0.35 Ag^{-1}. During long cycling at an elevated current density of 2 Ag^{-1}, the anode showed an initial discharge capacity of 572 $mAhg^{-1}$. It maintained a capacity of 399 $mAhg^{-1}$ by the 1360th cycle, with a very low capacity decay of 0.022% per cycle (Rao et al., 2024).

One notable example is $CuFeS_2$ QDs embedded in a carbon matrix. A study by Guo et al. illustrated that these QDs when used as anode materials, achieved a high reversible capacity of 760 $mAhg^{-1}$ while maintaining this capacity consistently for 700 cycles. This indicates high performance and superior cycling stability (Guo et al., 2017). Similarly, Shen et al. reported that Co_3O_4 QDs could enhance capacity and cycle life in lithium-ion batteries, reinforcing the significance of QDs in sustaining electrochemical reactions (Shen et al., 2022).

The study of GQDs described by Chao et al. also revealed that these QDs could enhance electrode durability. The research reported that GQDs-coated VO_2 electrodes displayed exceptional stability and 94% retention of the original capacity after 1500 cycles at 18 Ag^{-1}, showcasing the ability of QDs to maintain performance under demanding conditions (Chao et al., 2014). This long cycle life emphasizes the importance of a robust interface created by QDs, preventing the degradation of active materials.

Furthermore, Peng et al. designed CoO QD-graphene composites that achieved a capacity of 1306 $mAhg^{-1}$ after 100 cycles, highlighting the dual role of QDs in augmenting both the specific capacity and the structural integrity needed for long-term cycling stability (Peng et al., 2012). This performance is significant when considering the ongoing market demands for electric vehicles, where longevity and efficiency are essential.

A recent study investigated the use of doped GQDs as anode material. Ruiyi et al. developed an efficient synthesis method for lithium titanate/nitrogen and sulfur co-doped GQDs (LTO/N.S-GQDs) to serve as an anode in lithium-ion batteries. They emphasized the important contributions of sulfur and nitrogen co-doping to the material's performance. This anode exhibited outstanding electrochemical properties, achieving a specific discharge capacity of 254.2 $mAhg^{-1}$ at a rate of 0.1

C and 126.5 $mAhg^{-1}$ at a higher rate of 10 C. Notably, the retention test demonstrated impressive capacity retention of 96.9% after 2000 cycles at a rate of 2 C (Ruiyi et al., 2015).

In the study by Hu et al., a practical approach to suppressing lithium dendrite formation was developed by incorporating GQDs into the electrolyte. These GQDs serve as seeds on the electrode surface, promoting dense and uniform lithium nucleation by regulating the electric field and ion flux at the electrode-electrolyte interface. An in-situ Raman analysis confirmed the crucial role of GQDs in enabling dendrite-free lithium deposition. This increased the critical current for internal short circuits caused by lithium dendrites from 5.88 to 7.44 $mAcm^{-2}$. Additionally, the soft short circuit in batteries with an areal capacity of 3 $mAhcm^{-2}$ was eliminated at a current density of 3 $mAcm^{-2}$. High-loading lithium-sulfur batteries with high Coulombic efficiency were successfully achieved using an anolyte with GQDs for anode protection (Hu et al., 2020).

Lee et al. (2022) reported an innovative strategy for the design of ultra-small zinc sulfide (ZnS) QDs featuring polymorphic structures anchored onto a nitrogen-doped carbon matrix (ZnS-QD@NC as anode for LIBs). The pyro-synthesized electrode, containing QD particles embedded within the nitrogen-doped carbon matrix, demonstrated a remarkable reversible capacity of 620 $mAhg^{-1}$ over more than 500 cycles at a current density of 1 Ag^{-1}. Additionally, the study's results underscore the potential for creating electrode-active materials characterized by ultra-small particles, novel phases, and unique structural and morphological compositions, all of which contribute to distinctive electrochemical behavior suitable for applications in rechargeable batteries (Lee et al., 2022).

3.1.2. Sodium-Ion Batteries (SIBs)

Incorporating QDs into SIBs has garnered significant research interest due to their potential to enhance electrochemical performance, particularly regarding capacity and cycle life. Given the abundance and lower sodium cost, sodium-ion batteries are regarded as a promising alternative to lithium-ion batteries. Due to their unique properties, QDs are instrumental in improving electrode materials, helping to mitigate the challenges associated with the larger size of sodium ions compared to lithium ions.

Recent studies have shown that CQDs can significantly enhance the performance of SIBs. For instance, a study conducted by Shan-Li et al. revealed that incorporating CQDs substantially improved the electrochemical properties of sodium-ion battery anodes, achieving a reversible capacity of about 370 $mAhg^{-1}$ after 100 charge-discharge cycles. This remarkable capacity retention over successive cycles

illustrates how CQDs contribute to enhanced structural stability and improved ion transport (Shan-Li et al., 2024).

Additionally, another investigation found that integrating MoS_2 QDs within graphene frameworks increased electrical conductivity and a larger surface area. These enhancements together led to a capacity of 200 $mAhg^{-1}$ after 200 cycles (Wei et al., 2019). The synergy between the QDs and the supporting materials allows for better accommodation of sodium ions and facilitates more efficient ion transfer processes during charging cycles.

Huang et al. performed research that highlighted the potential of ferroelectric $Sn_2P_2S_6$ QDs to achieve a capacity performance of approximately 215 $mAhg^{-1}$ with a robust cycle life, maintaining substantial capacity stabilization even after 150 cycles (Huang et al., 2018). The ferroelectric properties are suggested to contribute to enhanced electrochemical kinetics, allowing for efficient sodium storage and retrieval.

A study by Lee et al. (2025) introduced a carbonate-based electrolyte designed for practical sodium metal batteries (SMBs) by incorporating NCQDs. The negatively charged NCQDs interact with sodium ions, reducing the interaction between solvent molecules and sodium ions. This electrolyte was thoroughly investigated as a proof of concept. The findings indicate that adding NCQDs to the carbonate-based electrolyte enhances coulombic efficiency, decreases sodium nucleation overpotential, and extends plating and stripping performance for up to 700 hours. Moreover, the NCQDs are vital in improving sodium ion mobility within the electrolyte and facilitating the formation of a robust and stable solid-electrolyte interphase (SEI) layer enriched with inorganic constituents. The NCQD-enhanced electrolyte, referred to as EDFNC, enables the sustainable operation of practical SMBs with various cathode materials, confirming that the EDFNC electrolyte is versatile and not confined to specific cathode types (Lee et al., 2025).

The investigation by Zhang et al. (2019) on bismuth nanodots revealed notable advancements in performance metrics. Incorporating QD structures into electrode designs achieved a capacity of 268 $mAhg^{-1}$ and a cycle retention rate exceeding 80% after 300 cycles. These results indicate a promising strategy to address the capacity degradation typically seen in standard sodium-ion batteries (Zhang et al., 2019). The smaller particle sizes and greater surface area of the nanodots afford enhanced ion accessibility and minimize diffusion paths for sodium ions, ultimately leading to improved overall battery performance.

3.2. Quantum Dots in Supercapacitors

QDs have been recognized for their significant role in enhancing the performance characteristics of supercapacitors, mainly focusing on energy density, power density, and cycle life. Their unique properties facilitate charge storage mechanisms that contribute to the overall improvement in supercapacitor performance.

One notable study by Xia et al. (2014) explored the synthesis of hematite quantum-dot/functionalized graphene-sheet composites utilized as advanced anode materials for asymmetric supercapacitors. This study revealed that the asymmetric configuration could achieve an impressive maximum energy density of 50.7 $Whkg^{-1}$, paired with a power density of 100 Wkg^{-1}. Such performance significantly surpasses traditional symmetric supercapacitors, highlighting the enhanced capabilities of QDs in energy storage applications (Xia et al., 2014).

In another study, Chen et al. developed a V_2O_5/biomass carbon nanocomposite using graphene QDs. Their findings indicated an energy density of 43.7 $Whkg^{-1}$ at a power density of 425 Wkg^{-1}, demonstrating the ability of QDs to optimize energy storage and power delivery in supercapacitor systems. Notably, even at elevated power densities, the energy density retained a commendable value of 31.025 $Whkg^{-1}$ at 2550 Wkg^{-1}, underscoring the effectiveness of QDs in maintaining performance across varying operational conditions (Chen et al., 2023).

The study carried out by Yang et al. has significantly advanced our understanding of the balance between power and energy densities in energy storage systems. They reported energy densities within the 1.36 to 25.68 mWh cm^{-3}, emphasizing that supercapacitors incorporating QDs significantly improve over traditional systems (Yang et al., 2017). These results illustrate the capacity of QDs to enhance volumetric energy storage, which is vital for practical applications in energy storage devices.

Additionally, further advancements by Lakshmi-Narayana et al. focused on the use of $NiCo_2O_4$/GQDs (Fig. 6), leading to enhanced performance metrics with an energy density of 69.5 Wh kg^{-1} and a power density of 2.2 $kWkg^{-1}$. The ability of this asymmetric supercapacitor to sustain such high energy values highlights the potential of QDs to promote superior electrochemical properties and efficient charge transfer mechanisms (Lakshmi-Narayana et al., 2024).

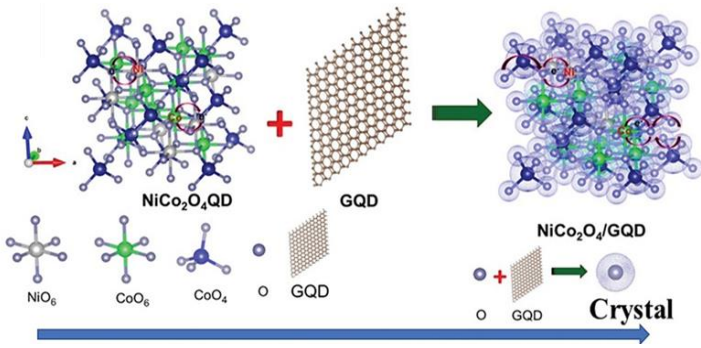

Figure 6. Formation of $NiCo_2O_4$/GQDs (Lakshmi-Narayana et al., 2024). Reproduced with permission from Wiley, Copyright 2024.

Gao et al. (2024) noted that GQDs-based supercapacitors exhibited operational stabilities exceeding 100000 cycles, a crucial factor for applications requiring durability and reliability in energy storage technologies. Moreover, Liu et al. (2013) affirmed that micro-supercapacitors based on QDs could operate effectively while maintaining rapid charge and discharge rates, contributing to lifespans that exceed millions of cycles.

Zhang et al. (2019) illustrated the performance potential of silver-quantum-dot-modified films, which achieved an energy density of 51.89 $Whkg^{-1}$ while maintaining a power density threshold of approximately 22.6 Wkg^{-1}. These films demonstrated excellent cycling performance, retaining significant energy storage efficiency over numerous cycles.

Additionally, the integration of QDs into flexible supercapacitors has been explored. A study by Xu et al. (2020) demonstrated $Ti_3C_2T_x$ QDs within a network structure, enabling exceptional energy storage capabilities (Fig. 7). This underscores the importance of QD interlayers in enhancing cycle-life stability. Such innovations enable high capacitive performance and longevity, ensuring that devices maintain operational integrity over extended use.

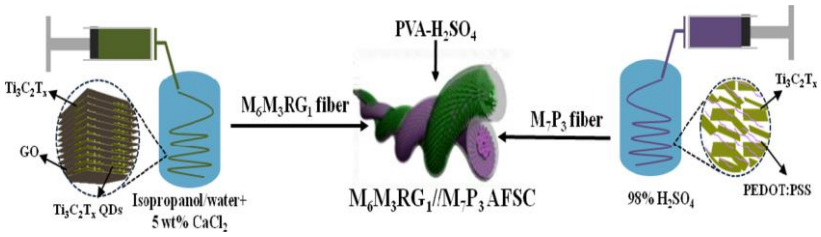

Figure 7. Schematic illustration of the preparation of all-solid-state asymmetric fiber supercapacitors (Xu et al., 2020). Reprinted with permission from the American Chemical Society.

3.3. Quantum Dots in Solar Cells

Integrating QDs into solar cells represents a notable advancement in photovoltaic technology, leading to enhanced performance metrics such as increased efficiency, improved light absorption, and excellent stability. The unique tunable band gaps and high absorption coefficients of QDs facilitate innovative designs that effectively address the limitations of traditional solar cells.

A key advantage of quantum dot-sensitized solar cells (QDSSCs) is their exceptional ability to absorb light within the visible spectrum. Rahayu and Lee (2024) demonstrated that by employing a straightforward successive ionic layer adsorption and reaction method, they achieved significant photovoltaic performance with CdSe QDSSCs. Their study emphasized the relationship between the number of SILAR cycles and both optical properties and photovoltaic efficiency. This work emphasizes the potential of QDs to provide highly tunable optical characteristics, thereby enhancing light harvesting capabilities.

Furthermore, the hybridization of QDs with existing semiconductor structures has proven to boost overall cell performance. Jung et al. noted that integrating ZnSe QDs with silicon nanowire solar cells increased light absorption, leveraging refractive index matching and optical confinement effects (Jung et al., 2012). This combination enhances the ability to capture low-energy photons, improving conversion efficiencies.

QDs facilitate the advancement of intermediate band solar cells (IBSC), which are theoretically capable of achieving efficiencies that surpass traditional limits. Ankhi et al. highlighted the potential for InGaAs/GaAs QD solar cells to reach conversion efficiencies close to 45% by employing intermediate band concepts, marking a significant enhancement over the established Shockley-Queisser limit (Ankhi et al., 2020). Integrating these structures will capture a broader solar energy spectrum, improving overall performance.

Du et al. conducted research that achieved a certified power conversion efficiency (PCE) of 11.6% in Zn–Cu–In–Se QD solar cells. This efficiency is among the highest reported for QD-based cells, underscoring the material's potential across various photovoltaic applications (Du et al., 2016). This impressive efficiency is attributed to the advantageous band structure and charge carrier dynamics facilitated by the QDs.

The effect of QD size on solar cell performance has been investigated by Wang et al. (2015), who discovered that smaller QDs can yield higher open-circuit voltages and increased short-circuit currents. This finding suggests that optimizing QD size is crucial for maximizing solar cell efficiency (Wang et al., 2015). Furthermore, other studies emphasize the significance of bandgap engineering through QD design to enhance light absorption and electron transport properties (Pan et al., 2018).

Recent studies on the stability of QD-based solar cells also highlight their robustness. Kim et al. (2012) observed that hybrid solar cells exhibit more excellent resistance to corrosion and leakage currents, which are prevalent issues in conventional liquid junction cells (Kim et al., 2012). The study confirmed the durability of cell performance over extended periods, reinforcing the potential of QD systems for long-term applications.

4. Advances in Quantum Dot Integration for Superior Energy Storage

Integrating QDs into energy storage systems signifies a significant advancement in materials science, mainly due to their unique optical and electrical properties. QDs, or semiconductor nanocrystals, range in size from 1 to 10 nanometers and exhibit quantum confinement effects that grant them tailored electronic and photonic properties. This size tunability and the associated properties facilitate their application in high-efficiency energy storage technologies, such as supercapacitors and batteries, enhancing overall performance through improved charge storage capabilities and charge transfer efficiency (Xu et al., 2022).

Recent advancements in the synthesis and application of QDs for electrochemical energy storage have received recognition. Specifically, the large specific surface area, adjustable energy levels, and favorable photoluminescence properties of QDs play crucial roles in optimizing charge storage performance. These characteristics enable higher charge densities and contribute to faster charge-discharge rates, desirable traits for energy storage applications. Both Chen et al. and Hu et al. emphasize the dual role of QDs in energy conversion and storage, as they act not only as active materials but also as mediators for electron transfer within composite electrodes (Hu et al., 2021; Arora et al., 2024).

Further exploring their structural properties, various types of QDs, including GQDs, CQDs, and hybrid materials, have demonstrated an ability to enhance the performance of energy storage devices. GQDs, in particular, combine the characteristics of both QDs and graphene, offering exceptional electrical conductivity, a high surface area, and excellent solubility in solvents, making them attractive candidates for applications in energy storage technologies (Ansari, 2022; Zahir et al., 2021). Incorporating these materials into electrode matrices has improved supercapacitor performance by enhancing charge transfer kinetics and surface reactivity, thus achieving higher capacitance values than traditional materials (Gao et al., 2024).

Additionally, integrating QDs into polymer composites is promising for energy storage applications. These composites utilize the distinct properties of QDs to improve electrochemical performance while tackling issues related to scalability and cost-effectiveness. Recent research has found that adding QDs to polymer matrices

enhances the dispersion and stability of active materials, leading to electrodes with enhanced mechanical and electrical characteristics (Das et al., 2022). The study emphasizes the importance of optimizing the structure of these nanocomposites to boost their performance by carefully adjusting the interactions between the various components (Shen et al., 2020).

Moreover, using QDs in supercapacitors, especially within hybrid systems that incorporate traditional materials like nickel sulfide or carbon-based elements, has led to notable enhancements in energy density and cycling stability. For example, the inclusion of carbon QDs in nickel sulfide matrices has been shown to boost electrocatalytic activity and overall supercapacitive performance in these composites (Sahoo et al., 2018). These improvements not only elevate energy storage efficiency but also extend lifespan and enhance reliability—key factors for commercial applications.

Research on charge storage mechanisms related to QDs reveals their effectiveness across various conditions, such as different pH levels and environmental contexts, demonstrating their adaptability and strength (Breczko et al., 2024). The advancement of core-shell structures like indium phosphide/zinc sulfide (InP/ZnS) QDs has opened up possibilities for innovative materials capable of preserving and managing charge storage for nonvolatile memory applications. Their capacity to confine charge carriers within the QD core further indicates their significance in memory systems aimed at efficient data storage (Hu et al., 2021)

At the same time, investigating biodegradable or non-toxic QDs sourced from biomass waste emphasizes a growing trend in environmentally sustainable energy storage solutions. This innovative strategy increases the value of waste materials and supports the circular economy while enhancing the efficiency of energy storage devices (Wu et al., 2023). By integrating renewable resources and advanced nanomaterial properties, the sector is underscored by the potential for significant advancements in energy technology.

As QDs evolve rapidly and gain attention in electrochemical energy storage, challenges remain regarding the scalability of their synthesis methods and the stability of materials enhanced by QDs under operational conditions. Ongoing research is essential to address these issues, enabling QD-enhanced energy storage systems to transition from laboratory tests to commercial applications (Wu et al., 2018).

These advancements in QD integration present opportunities for improved overall performance in energy storage devices and establish a foundation for innovations in energy conversion technologies. The path toward achieving efficient and sustainable energy storage solutions becomes clearer by further exploring the applications of QDs across various platforms, along with advancements in

nanotechnology and materials science. (Yang & Valdiviezo, 2024).In summary, the ongoing enhancement of QD technology, particularly in energy storage applications, presents exciting opportunities for creating next-generation batteries and supercapacitors. As this area progresses, significant investment in research and development will be essential to realize the full potential of QDs, leading to innovative approaches that improve energy efficiency and sustainability in our increasingly clean, energy-dependent world (Xu et al., 2022; Mousavi et al., 2022).

5. Quantum Dots Challenges, Limitations, and Proposed Solutions

QDs have emerged as a pivotal technology in various fields, such as optoelectronics, biomedical applications, and environmental sensing. However, their development poses numerous challenges and limitations that must be addressed to realize their full potential. Current research identifies key obstacles related to stability, toxicity, production methods, and integration with other technologies while proposing several innovative solutions.

One of the most significant challenges QDs face, mainly when utilized in light-emitting diodes (LEDs), is their efficiency and stability. For instance, perovskite QD LEDs have shown impressive external quantum efficiencies (EQE) exceeding 20% for several colors, including green, red, and near-infrared. However, the quest for efficient blue light-emitting perovskite QD LEDs continues to encounter hurdles, primarily due to difficulties in achieving stable blue luminescence, which is compounded by the need for efficient mixing of halides, such as chlorine and bromine, to optimize the emission color without sacrificing stability (Xiaofeng, 2024). This instability prohibits widespread commercial application, emphasizing the need for further research into more robust materials and configurations.

Furthermore, the issue of potential cytotoxicity is paramount regarding QDs composed of traditional heavy metals, particularly among II-VI compounds like CdSe or CdTe, which pose considerable health risks in biomedical applications. Documented evidence shows that the cytotoxicity of these semiconductor QDs has significantly limited their use in biological systems (Zhao et al., 2017). As an alternative, there is growing interest in developing silicon-based QDs, which have demonstrated significantly lower toxicity profiles and biocompatibility, making them suitable for biomedical applications (Erogbogbo et al., 2011). Despite these advancements, the urgent need for re-evaluation and innovation is critical to creating biocompatible materials that can reliably be used for long-term applications in living organisms.

The synthesis methods for QDs also present challenges. Current techniques often lead to particle size and shape variability, which directly influences their optical properties and stability. While traditional top-down fabrication methods can yield

higher purity QDs, they are generally more complex and time-consuming, thus limiting scalability (Devi & Tharmaraj, 2021). Conversely, bottom-up synthesis approaches, such as chemical vapor deposition, may produce QDs that are easier to scale but often suffer from size and ligand capping inconsistencies, affecting stability and functionality (Dai et al., 2017). Developing standardization in synthesis methods could mitigate these disparities and enhance the reproducibility of QD-based devices.

Another significant challenge is the integration of QDs with existing technologies. In the context of QLEDs, there is a continuous need to improve hole injection efficiency into the QD layers, as inadequate hole transport can severely limit device performance (Cao et al., 2018). Integration strategies that tailor QD energy structures to ensure compatibility with hole transport materials have been suggested as essential steps toward improving these devices' operational longevity and efficiency. Furthermore, developing novel materials alongside QDs may yield more effective charge transport mechanisms, leading to better overall performance in applications requiring high-efficiency devices (Dai et al., 2017).

In the biomedical realm, the delivery of QDs across cell membranes remains a pressing issue. Studies in recent years indicate that while QDs can function brilliantly as imaging markers or therapeutic agents, their application is hampered by difficulties in efficiently delivering them to desired cellular locations (Jablonski et al., 2010). Advancements in bioconjugation techniques and the development of more sophisticated delivery systems, such as biodegradable carriers, are essential for improving the cellular uptake of QDs (Rosenthal et al., 2011). Moreover, emerging strategies that enhance biocompatibility through surface modifications could lead to more effective cellular interactions, potentially overcoming current barriers to their use in imaging and therapy.

As QDs are increasingly utilized in environmental sensing applications, their stability and durability in varying conditions are critical for reliable field deployment. The lack of robust stability, particularly in fluctuating environmental conditions, can hinder their real-time sensing capabilities (Wang et al., 2022). Researchers are advocating for incorporating auxiliary materials that can encapsulate QDs, thus enhancing their resilience against environmental degradation while maintaining the activity and functionality of the QDs (Deepika et al., 2019).

Despite these challenges, numerous pathways for innovation and improvement exist. Developing carbon-based QDs represents one exciting avenue that circumvents many toxicity concerns related to heavy metal-based QDs. Such material advancements promise eco-friendly options while maintaining or enhancing the desirable optical properties inherent in traditional QDs. The broad and highly tunable photophysical properties of carbon dots could enable their application in

diverse fields, including but not limited to photonics, biomedicine, and environmental sensing (Wang et al., 2024).

While the challenges associated with QDs are multifaceted and complex, targeted research efforts are directed toward understanding their limitations and formulating effective solutions. The continuous evolution of materials science, synthesis methodologies, and application-oriented research will provide a more straightforward path for the eventual commercialization and integration of QD technology across various sectors.

As QDs progress, interdisciplinary collaboration will be essential. Bridging gaps between materials science, chemistry, biology, and engineering can yield comprehensive solutions that further harness the unique properties of QDs. Nurturing this collaborative spirit may not only solve existing problems but also uncover new possibilities in the realm of QD applications, paving the way for innovations that can significantly impact industry and medicine alike.

6. Future Perspectives and Research Directions

QDs have emerged as promising nanomaterials for applications in optoelectronics, energy harvesting, and biosensing. Despite their remarkable properties, challenges related to large-scale production, stability, and efficiency hinder their widespread commercialization. This chapter explores key future research directions, including synthesis optimization, stability enhancement, functionalization strategies, and advanced applications in energy storage and biomedical fields. Addressing these challenges will facilitate the integration of QDs into next-generation nanodevices and sustainable energy solutions.

One significant obstacle in QD research is the development of cost-effective and scalable synthesis methods. Current approaches, including top-down and bottom-up strategies, often produce particle size and composition inconsistencies. Future research should focus on refining these methods to ensure uniformity in structural and functional properties, enhancing their suitability for industrial applications (Ghosh et al., 2021).

Environmental considerations also play a vital role in the future perspectives of QDs in energy applications. The renewable synthesis of QDs from biomass offers a sustainable alternative to traditional methods, as discussed by He, where eco-friendly strategies can enhance QDs' properties and functionalities while reducing environmental impact (He, 2023). This aligns with global movements towards sustainable energy solutions, where materials with low toxicity and environmental footprint, such as GQDs, are increasingly prioritized (Ansari, 2022).

Long-term stability remains a key concern for QD-based devices. Surface passivation and encapsulation strategies must be explored to improve photostability,

chemical resistance, and overall durability (Ghosh et al., 2021). Additionally, research should focus on developing sustainable and eco-friendly synthesis techniques to minimize environmental impact.

Doping, heterostructuring, and functionalization are promising approaches to enhance the optical and electronic properties of QDs. For instance, nitrogen-doped GQDs have demonstrated improved charge transport, making them highly suitable for photodetectors and solar cells (Tang et al., 2014). Future studies should explore the impact of various dopants and hybrid structures to maximize energy efficiency.

Moreover, exploring QD heterostructures is an exciting avenue in energy storage research. The van der Waals heterojunctions formed between different quantum materials enable unique electronic properties that can be harnessed for photoelectrochemical energy conversion, as suggested by Yan et al. (Yan et al., 2020). These heterojunctions and hybrid structures could significantly improve the electrochemical performance of existing energy storage technologies by enhancing charge extraction and transport mechanisms.

QDs exhibit potential in energy storage applications, including supercapacitors and lithium-ion batteries. By incorporating these materials with advanced electrode architectures, researchers can enhance charge storage capacity, cycling stability, and overall energy density. Moreover, further exploration is needed into their role in flexible and wearable energy storage technologies.

Hybrid materials incorporating QDs with other nanomaterials, such as metal-organic frameworks (MOFs), perovskites, and conductive polymers, have the potential to create highly efficient multifunctional devices. These hybrid materials can enhance energy storage capacity, improve optoelectronic performance, and enable novel applications in flexible and wearable electronics. Future research should explore scalable fabrication techniques and investigate the stability and efficiency of these hybrid systems under real-world conditions.

Beyond energy applications, QDs hold promise for biomedical imaging, drug delivery, and environmental monitoring. Their biocompatibility and tunable fluorescence properties enable targeted imaging and theranostics (Yang et al., 2023). Research should focus on multifunctional QD-based platforms for real-time biosensing and pollutant detection.

The future of QDs in energy storage systems is undeniably promising, with abundant opportunities ripe for exploration. Significant advancements in synthesis methods, the development of heterostructures, sustainable manufacturing practices, and the integration of QDs into hybrid systems are all key components in optimizing energy storage solutions. As researchers aggressively pursue the potential of QDs, their critical role in enhancing efficiency, capacity, and sustainability in energy storage technologies will be essential to meet the escalating global energy demands.

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Bölüm 4

2-İzopropil-5- Metilfenoksi Ftalosiyanin Grup Temelli Potansiyometrik Gümüş-Seçici Sensör ve Durgun Ortamdaki Potansiyometrik Performans Özellikleri

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Özet

İnsan dokularındaki gümüş miktarı düşüktür. Ancak aşırı maruz kalma, ciltte, karaciğerde, böbreklerde, mukoza zarlarında, kornealarda, diş etlerinde, dalakta ve tırnaklarda gümüş birikmesine neden olabilir [1]. Gümüşe maruz kalma, yutma, solunum ve deri yoluyla maruz kalma gibi çeşitli mekanizmalar yoluyla meydana gelebilir [2-3]. Yaklaşık 50 mg'lık intravenöz bir gümüş dozu ölümcül kabul edilir ve kemik iliği, böbrek ve karaciğer nekrozu, kanama ve pulmoner ödemle sonuçlanır. Gümüş kanserojen olarak kabul edilmese de genotoksik etkiler bildirilmiştir. Gümüş toksisitesinin tedavisi için bilinen etkili bir şelatör bulunmamaktadır [3]. Kandaki gümüş miktarı, gümüşe sürekli maruz kalındığında artar ve kalbin genişlemesi ve anemi gibi yan etkilere neden olur. Bu nedenle gümüş tayini önemlidir [4]. Gümüş tayini için birçok analitik yöntem geliştirilmiştir. Fakat çoğu, pahalı cihazlar gerektirmekte ve analizi

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zaman almaktadır. Gümüş iyonlarının hızlı, ucuz ve basit bir şekilde tayin edilmesi klinik ve çevre analizlerinde oldukça önemlidir. Potansiyometrik yöntem ucuz, basit ve hızlı bir yöntemdir. Gümüş iyonunun tayini için birçok potansiyometrik yöntem geliştirilmiştir. Sensörlerde kullanılan iyonoforların pahalı olmasından dolayı yeni iyonoforların belirlenmesi önem kazanmaktadır. Çalışmamızda kullanılan Tetrakis 2-izopropil-5- metilfenoksi ftalosiyaninato Çinko (II) bileşiği iyonofor olarak pahalı ticari iyonoforlara alternatif olarak düşünülmektedir. Bu çalışmada, Tetrakis 2-izopropil-5- metilfenoksi ftalosiyaninato Çinko(II) bileşiği iyonofor olarak kullanılarak Ag^{+}–seçici PVC membran potansiyometrik elektrot geliştirildi ve durgun ortamda potansiyometrik performans özellikleri araştırıldı. Optimum membran bileşimi olarak %3 Tetrakis 2-izopropil-5- metilfenoksi ftalosiyaninato Çinko(II), %32 PVC, %64 DBF ve %1 KTPClPB membran bileşimi belirlendi. Bu elektrodun $5x10^{-6}$ M – 10^{-1} M konsantrasyon aralığında on katlık konsantrasyon değişiminde 63 mV'luk eğimle (R^2 = 0,9995) doğrusal bir cevap sergiledi. Elektrodun cevap zamanı, 15s olarak belirlendi. Elektrodun pH çalışma aralığı pH=4,5-6,5 olarak belirlendi.

1. Giriş

Fiziksel özellik açısından yoğunluğu 5 g/cm^3 ten daha yüksek olan metaller için ağır metal terimi kullanılır. En önemli ağır metallerden biri gümüştür. Bu metal, diğer tüm metallerle karşılaştırıldığında en iyi elektriksel ve termal iletkenliğe ve yansıtma özelliğine sahiptir [2-4]. Bu özellikler toplumda çok çeşitli kullanım ve uygulamalar sağlar. İnsanların gümüşe maruz kalması yüzyıllardır gerçekleşmektedir ve antik medeniyetlere kadar uzanmaktadır. Gümüşe maruz kalma, endüstri, mesleki maruziyet, ilaçlar ve besin takviyeleri yoluyla gerçekleşir. Gümüşe tekrarlanan veya uzun süreli maruz kalma, gümüş toksisitesine yol açabilir [5]. Hem değerli hem de endüstriyel bir metal olan geçiş metali gümüş, 2012'de tahmini 24.000 ton üretimle çıkarılmakta ve geniş bir uygulama yelpazesine sahiptir. Gümüş, polimer kimyasında, dayanıklılığı artırmak amacıyla, ayna yapımı, elektronik cihazlarda, kaplamacılıkta, kuyumculuk ve fotoğrafçılıkta, para yapımında, batarya ve pillerde, antimikrobiyal tekstil üretiminde, suların dezenfeksiyonunda ve medikal uygulamalarda, lehim ve kaynaklarda, katalizör olarak kullanılabilir. Ayrıca, gümüşün geniş spektrumlu antimikrobiyal etkileri de rapor edilmiştir. Antik Yunanlılar bile gümüş preparatlarını ülserlerin tedavisi, yara iyileşmesini teşvik etmek, yiyecek ve su için koruyucu olarak kullanmışlardır [6]. Aslında, gümüş 1940'larda antibiyotiklerin tanıtılmasından önce en önemli antimikrobiyal madde olarak kullanılmıştır. Antibakteriyel etkileri ve insan hücreleri için düşük

toksisitesi nedeniyle bugün hala çok çeşitli tıbbi uygulamalarda kullanılmaktadır. Örneğin arasında yanık yaralarının tedavisinde topikal krem olarak gümüş preparatlarının kullanımı [7], diş amalgamlarında, koruyucu göz bakımında, kateterler ve kalp kapakçıkları gibi tıbbi cihazlarda bakteri (biyofilm) büyümesini önlemek için gümüş emdirilmiş polimerlerin kullanımı yer alır. Gümüş ayrıca yüzme havuzu suyu, hastane sıcak su sistemleri ve içme suyu sistemleri gibi su sistemlerinin dezenfektanı olarak yaygın olarak kullanılır. Bu amaçlar için gümüşün, suyun rengi, tadı ve kokusu üzerinde olumsuz bir etkisinin olmaması gibi avantajları vardır [8]. Gümüş, çamaşır deterjanlarına alternatif olarak bile kullanılmaktadır [9]. Antibiyotik dirençli suşların görülme sıklığındaki ve sayısındaki artış, gümüşün ve bileşiklerinin antimikrobiyal etkilerine olan ilgiyi yeniden canlandırdı. Gümüş nanopartiküller antioksidan özellikleri nedeniyle kanser veya dejeneratif Alzheimer hastalığının tedavisinde bir potansiyele sahiptir [10-12]. Son zamanlarda yara bakım ürünleri, tıbbi cihazlar, tekstil, kozmetik ve ev aletlerinde antibakteriyel ve antifungal ajanlarda gümüşün kullanımında büyük bir artış olmuştur ([13, 14]. Ancak, gümüş bileşiklerinin aşırı klinik kullanımının gümüşe dirençli bakterilere yol açıp açmayacağı konusunda endişeler dile getirilmektedir [13-15]. Gümüş bileşiklerine uzun süreli maruz kalmayla ilişkili en yaygın gözlemlenebilir değişiklikler, sırasıyla ciltte ve gözlerde gümüş selenit ve gümüş sülfit çökeltilerinin geri döndürülemez bir şekilde birikmesiyle karakterize edilen argyria ve argyrosis'tir. Etkilenen bölge mavimsi gri olur ve güneş ışığının varlığında daha da kötüleşir [1, 16, 17]. Gümüşün tıbbi kullanımları arasında, koterizasyon için gümüş nitrat ve yanıklar ile yaraların topikal tedavisi için gümüş sülfadiazin bulunur. Gümüş katyonlarının çok düşük seviyeleri, yara ve yanık tedavisinde etkili olan mikrobisit özelliklere sahiptir. Tıbbi cihaz kateterleri de mikrobiyal büyümeyi önlemek için gümüşle kaplanmaktadır [13]. Gümüşün antimikrobiyal özelliğinin, gümüş iyonlarının bakteriyel zarlarla birleşerek onları kalıcı olarak tahrip etme yeteneğiyle ilişkili olduğu hipotez edilmektedir [18]. Gümüş toksisitesinin komplikasyonları arasında dermatolojik, kardiyovasküler, hematolojik, hepatik, gastrointestinal, nörolojik ve renal bulgular yer alır [19]. Dünya Sağlık Örgütü, yaklaşık olarak 10 g gümüşün ömür boyu alımının insanda gözlemlenebilir olumsuz etki seviyesi olarak kabul edilebileceğine karar vermiştir [20]. Fabrika atıklarından kaynaklanan gümüş kalıntılarının bulunduğu aşırı kirli bölgelerde yaşayan kişilerde (örn. San Francisco Körfezi) gümüşün besin zincirine girmesiyle arjiri hastalığı geliştirme riski de artmaktadır [21]. İnsan dokularındaki gümüş miktarı düşüktür. Ancak aşırı maruz kalma, ciltte, karaciğerde, böbreklerde, mukoza zarlarında, kornealarda, diş etlerinde, dalakta ve tırnaklarda gümüş birikmesine

neden olabilir [1]. Gümüşe maruz kalma, yutma, solunum ve deri yoluyla maruz kalma gibi çeşitli mekanizmalar yoluyla meydana gelebilir [2, 3]. Yaklaşık 50 mg'lık intravenöz bir gümüş dozu ölümcül kabul edilir ve kemik iliği, böbrek ve karaciğer nekrozu, kanama ve pulmoner ödemle sonuçlanır. Gümüş kanserojen olarak kabul edilmese de genotoksik etkiler bildirilmiştir. Gümüş toksisitesinin tedavisi için bilinen etkili bir şelatör bulunmamaktadır [3]. Gümüş tayini için voltametri [22-28] spektrofotometri ([29-35], yüksek performanslı sıvı kromotografisi [36, 37] yöntemleri geliştirilmiştir. Bu yöntemlerde kullanılan ekipmanlar pahalı, zaman alıcı, uzman ve ön işlem gerektirdiğinden daha basit, ucuz, uzman gerektirmeyen iyon seçici elektrotların kullanıldığı potansiyometrik yöntem bu çalışmada kullanılmıştır.

Bu çalışmada, tetrakis 2-izopropil-5- metilfenoksi ftalosiyaninato çinko (II) bileşiği iyonofor olarak kullanılarak PVC membran Ag^{+}–seçici elektrot geliştirilmesi ve durgun ortamda potansiyometrik performans özellikleri araştırıldı.

2. Materyal ve Metod

2.1. Materyal

Tetrahidrofuran (THF), yüksek molekül ağırlıklı polivinilklorür (PVC), o-nitrofeniloktileter (NPOE), Dibütilftalat (DBF) ve KTpClPB Sigma-Aldrich firmasından temin edildi. $ZnCl_2$, Çalışmada kullanılan bütün diğer tuzlar Sigma-Aldrich firmasından sağlandı. Ölçümler süresince referans elektrot olarak Ag/AgCl elektrot (Gamry) kullanıldı.

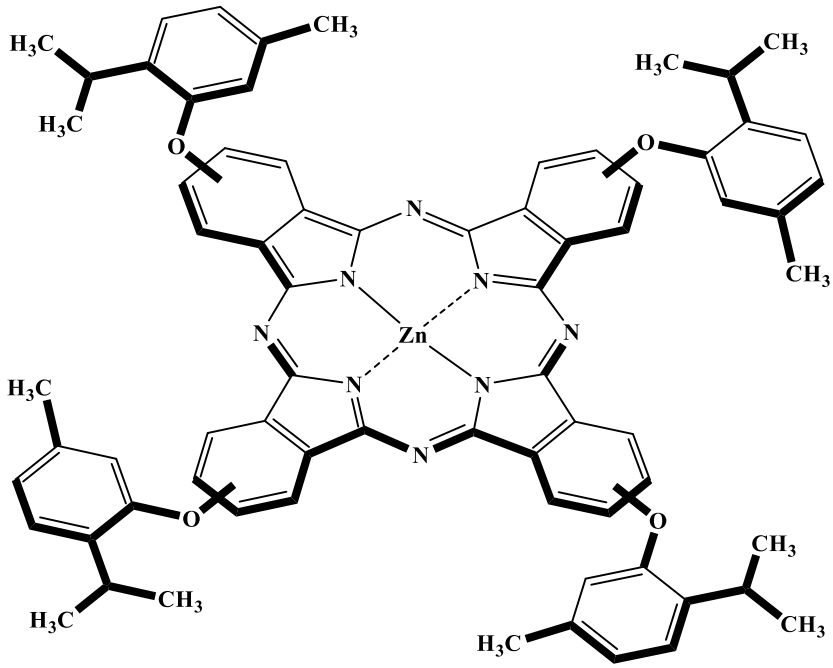
2.2. Cihazlar

Potansiyometrik ölçümler, bilgisayar kontrollü 4 kanallı Potansiyometre (ISEDO) kullanıldı. Potansiyel ölçümlerinin tümünde referans elektrot olarak GAMRY firmasından temin edilen Ag/AgCl referans elektrodu kullanıldı. Tartım işlemlerinde, RADWAG marka analitik hassas terazisi kullanıldı. Çalışılan çözeltilerin pH ölçümü İSTEK marka pH ölçüm cihazı ile yapıldı. Çözeltilerin hazırlanmasında kullanılan deiyonize su, Human Power I marka deiyonize su cihazından temin edildi.

2.3. 2,10,16,24-Tetrakis (2-izopropil-5-metilfenoksi ftalosiyaninato) Çinko (II) Sentezi [38]

4-(2-izopropil-5-metilfenoksi) ftalonitril [38] (0,100 g, 0,36 mmol) ve $ZnCl_2$ (0,020 g) karışımı bir kuvars pota içinde toz haline getirildi ve 200 °C'de nitrojen atmosferinde 7 dakika boyunca kapalı bir cam tüpte ısıtıldı. Oda sıcaklığına soğutulduktan sonra, ürün soğuk, sıcak etanol ve n-heksan ile

yıkandı ve süzüldü. Ürün, safsızlıkları gidermek için THF'de çözüldü.Spektral veriler yapıyı doğrulamaktadır [38].



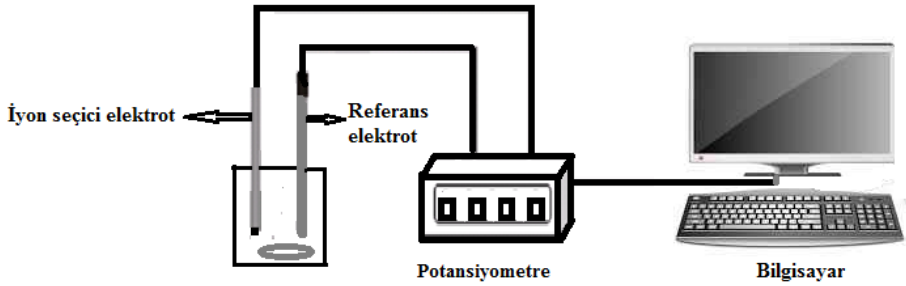
Şekil 1. 2,10,16,24-Tetrakis(2-izopropil-5-metilfenoksi ftalosiyaninato) Çinko(II)

2.4. Katı kontaktların hazırlanması

0,5g grafit, 0,35g epoxy ve 0,15g sertleştiricinin üzerine 1,5 mL THF eklenip sürekli karıştırılmasıyla hazırlandı.

2.5. Ftalosiyanin Temelli PVC membran Ag^+ Seçici Elektrotların Hazırlanması

Etrafı izole edilmiş bakır telin açık ucu önce katı kontakta daldırılarak 24 saat kurutuldu. İyonofor olarak Tetrakis 2-izopropil-5- metilfenoksi ftalosiyaninato Çinko (II) kullanılarak 4 farklı kompozisyonda hazırlanan membran bileşimleri, 1 mL THF'de çözülerek membran çözeltileri hazırlandı. Katı kontakt ile kaplanan kısım 5 kez membran çözeltisine daldırılarak membran ile kaplandı. Elektrotlar 24 saat oda koşullarında kurutulduktan sonra 10^{-2} $molL^{-1}$ $AgNO_3$ çözeltisinde 12 saat koşullandırıldı. Çalışılan membran bileşimleri ve potansiyometrik performans özellikleri Tablo 1'de detaylı olarak verilmiştir.



Şekil 2. Potansiyometrik ölçümlerde kullanılan potansiyometrik sistem

3. Bulgular ve Tartışma

3.1. Sensörlerin Membran Bileşimleri ve Doğrusal Çalışma Aralıkları

Membran bileşimi, bir iyon-seçici elektrodun potansiyometrik performans özelliğini büyük ölçüde etkilemektedir. Değişik oranlarda ve türde iyonofor, plastikleştirici, iyonikleştirici ve PVC oranları ile 4 farklı elektrot elde edildi ve en iyi performansı sergileyen elektrot belirlendi. Ag^{+}-seçici elektrodun geliştirilmesi amacıyla hazırlanan membran bileşimleri Tablo 1'de ve ve bunlara ait potansiyometrik performans özellikleri Tablo 2'de verilmiştir.

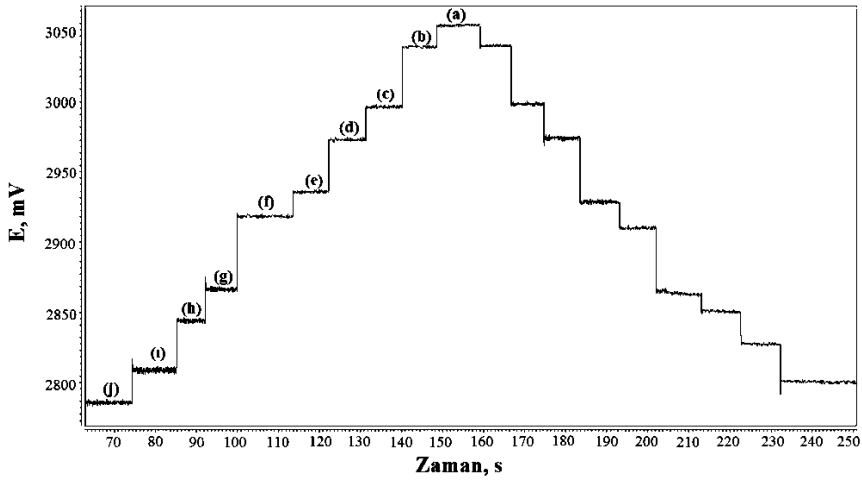
Tablo 1. Çalışılan membran bileşimleri ve potansiyometrik performans özellikleri

Elektrot No	Kompozisyon Bileşimi (%)				
	İyonofor	PVC	NPOE	DBF	KTpClPB
A1	3	32	65	-	-
A2	3	32	64	-	1
A3	3	32	-	65	-
A4	**3**	**32**	**-**	**64**	**1**

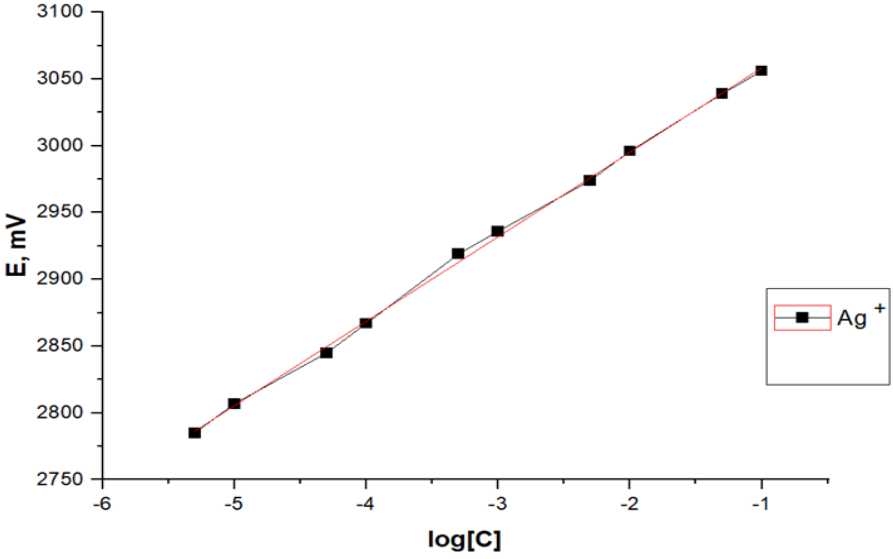
Tablo 2. Potansiyometrik performans özellikleri

Elektrot No	**Eğim (mV)**	**Doğrusal Çalışma Aralığı(molL^{-1})**	**R^2**	**Tayin Limiti (molL^{-1})**
A1	63	$5.0x10^{-5}$ –$1.0x10^{-1}$	0,9972	$5.0x10^{-5}$
A2	71	$5.0x10^{-5}$ –$1.0x10^{-1}$	0,9893	$5.0x10^{-5}$
A3	77	$1.0x10^{-4}$ M–$1.0x10^{-1}$	0,9988	$1.0x10^{-4}$
A4	**63**	**$5.0x10^{-6}$ –$1.0x10^{-1}$**	**0,9995**	**$5.0x10^{-6}$**

Optimum membran bileşimi, %3 (w/w) iyonofor (Tetrakis 2-izopropil-5-metilfenoksi ftalosiyaninato Çinko (II), %64 (w/w) plastikleştirici (DBF), %32 (w/w) polimer (PVC) ve %1 KTpClPB olarak bulundu. Bu bileşimle hazırlamış olduğumuz elektrot Ag^+-seçici elektrot olarak belirlendi.



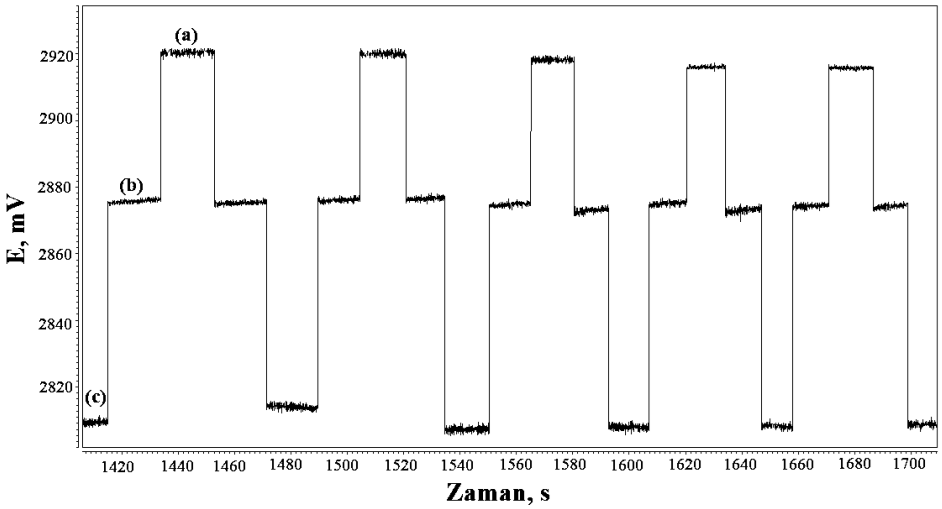
Şekil 2. A4 numaralı elektrodun Ag^+-seçici elektrodun Ag^+ iyonuna karşı durgun ortamdaki potansiyometrik davranışı. (a) 1×10^{-1} molL^{-1} (b) 5×10^{-2} molL^{-1} (c) 1×10^{-2} molL^{-1} (d) 5×10^{-3} molL^{-1} (e) 1×10^{-3} molL^{-1} (f) 5×10^{-4} molL^{-1} (g) 1×10^{-4} molL^{-1} (h) 5×10^{-5} molL^{-1} (ı) 1×10^{-5} molL^{-1} (j) 5×10^{-6} molL^{-1}



Şekil 3. Ag^+- seçici elektrotlar ile elde edilen kalibrasyon grafiği

3.2. Ag^+- Seçici Sensörün Tekrarlanabilirliği

Ag+ iyonu için Ag+- seçici sensör ile 10^{-2} molL^{-1}, 10^{-3} molL^{-1} ve 10^{-4} molL^{-1} $AgNO_3$ çözeltilerinde elde edilen tekrarlanabilirlik sonuçları Şekil 3 ve Tablo 3 'te verilmiştir.



Şekil 4. Ag+-seçici elektrodun 10^{-2} molL^{-1}, 10^{-3} molL^{-1} ve 10^{-4} molL^{-1} $AgNO_3$ çözeltilerinde tekrarlanabilirliği

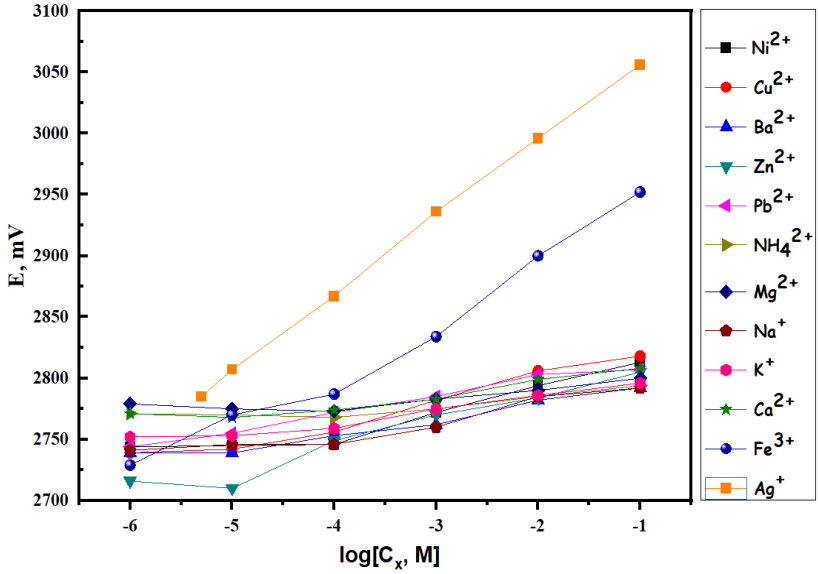
Tablo 3. Ag^+-seçici elektrodun $1.0x10^{-2}$ molL^{-1}, $1.0x10^{-3}$ molL^{-1}, $1.0x10^{-4}$ molL^{-1} Ag^+ iyonu için tekrarlanabilirlik sonuçları

Konsantrasyon (molL^{-1})	1. Ölçüm	2. Ölçüm	3. Ölçüm	4. Ölçüm	5. Ölçüm	x̄±S
$1.0x10^{-2}$ molL^{-1}	2920	2920	2919	2918	2918	2919.0±1.0
$1.0x10^{-3}$ molL^{-1}	2875	2876	2875	2875	2874	2875.0±0.7
$1.0x10^{-4}$ molL^{-1}	2812	2808	2808	2808	2809	2809.0±1.7

3.3. Ag^+- Seçici Sensörün Seçiciliği

İyon seçici elektrotların en önemli karakterizasyon parametrelerinden biri seçiciliktir. Seçicilik, önerilen bir iyon seçici elektrotun, ortamdaki diğer türlerden etkilenmeden tek bir türe özgü davranışıdır. Bu çalışmada, önerilen elektrotun seçiciliği IUPAC tarafından önerilen ayrı çözelti yöntemine (SSM) göre belirlendi ve seçicilik katsayıları hesaplandı [39]. Bu amaçla potansiyometrik ölçümlerden elde edilen veriler kullanılarak Tablo 2'de verilen iyonların $1{,}0\times10^{-2}$ M konsantrasyonunda sergiledikleri potansiyel değerleri

IUPAC tarafından önerilen denklemde yazılarak hesaplanmıştır. Gümüş(I)–seçici potansiyometrik elektrotun seçicilik katsayıları Tablo 2'de verilmiştir.



Şekil 5. Ag^+-seçici elektrodun Ag^+ ve diğer iyonlara karşı $1,0\times10^{-1}$ $molL^{-1}$-$1,0\times10^{-6}$ $molL^{-1}$ konsantrasyondaki diğer iyonlara karşı durgun ortamdaki potansiyometrik davranışı

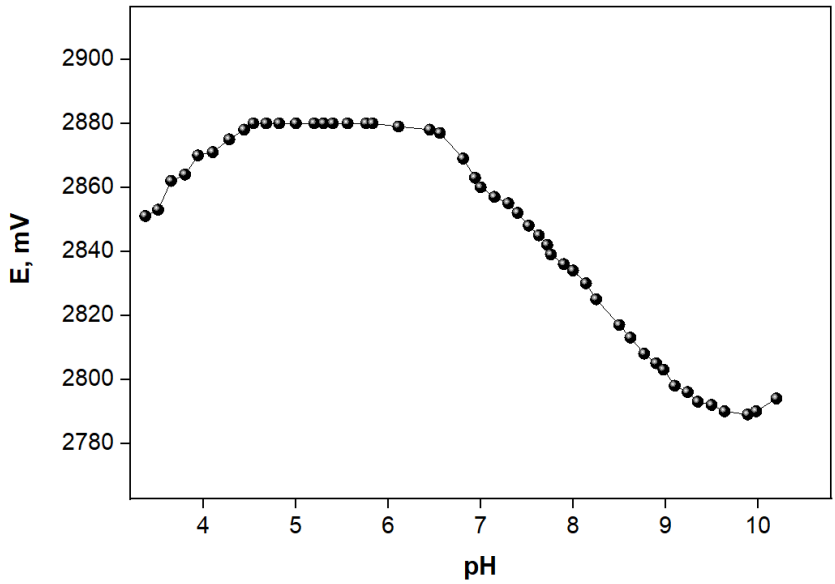
Tablo 4. Ag^+- seçici elektrotların seçicilik katsayıları

İyonlar	$K_{Ag+/B}$	-log $K_{Ag+/B}$
Fe^{3+}	$1,42x10^{-3}$	2,85
K^+	$4,86x10^{-4}$	3,31
Na^+	$4,69x10^{-4}$	3,33
NH_4^+	$4,69x10^{-4}$	3,33
Cu^{2+}	$1,08x10^{-4}$	3,97
Ba^{2+}	$1,01x10^{-4}$	3,99
Pb^{2+}	$9,03x10^{-5}$	4,04
Ca^{2+}	$7,81x10^{-5}$	4,11
Ni^{2+}	$6,51x10^{-5}$	4,19
Mg^{2+}	$5,62x10^{-5}$	4,25
Zn^{2+}	$4,52x10^{-5}$	4,34

3.4. Sensörün pH Çalışma Aralığı

Yapılan çalışmada $1,0x10^{-3}$ $molL^{-1}$ $AgNO_3$ çözeltisi içerisine 1,0 $molL^{-1}$ ve 0,1 $molL^{-1}$ HCl ile 1,0 $molL^{-1}$ ve 0,1 $molL^{-1}$ NaOH çözeltileri eklenerek pH'lar ayarlanarak ölçümler alındı. Ag^+-seçici elektrotun pH 4,5-6,5 aralığında ortamın

pH'sından etkilenmediği gözlendi. Ag^+ seçici elektrotların pH çalışma aralığını gösteren grafik Şekil 6.' da verilmiştir.



Şekil 6. Ag^+- seçici elektrodun pH çalışma aralığı

3.5. Ag^+- Seçici Sensör İle Numune Analizi

Gümüş- seçici elektrotlar ile yapılan, sentetik olarak hazırlanmış ve içerisinde her bir iyonun derişimi $1{,}0x10^{-2}$ $molL^{-1}$ olacak şekilde sabit tutulmuş farklı bileşimlerdeki sentetik numunelerin analizleri yapıldı. Elde edilen sonuçların memnun edici seviyede olduğu gözlendi. Tablo 5.' te sentetik numune analizi işlemlerinde kullanılan numunelerin bileşimleri ve belirlenen Ag^+ miktarları ($molL^{-1}$) ortalama ve standart sapmaları verilmiştir. Ortalama ve standart sapma değerleri n=5 için verilmiştir.

Tablo 5. Ag^+- seçici sensör ile yapılan sentetik numune analiz sonuçları

Sentetik Numune	**Numune Bileşimi ($1{,}0\times10^{-2}$ $molL^{-1}$)**	**Ag^+ miktarları ($molL^{-1}$)**
S-1	Ag^+ , K^+ , Na^+ , Ni^{2+}	$1{,}09(\pm0{,}35)\times10^{-2}$
S-2	Ag^+ , Na^+ , Mg^{2+} , Co^{2+}	$1{,}18(\pm0{,}20)\times10^{-2}$
S-3	Ag^+ , Ca^{2+} , NH_4^+ , Mg^{2+}	$1{,}13(\pm0{,}20)\times10^{-2}$

4. Tartışma ve Sonuç

Gümüş tayini için tetrakis 2-izopropil-5- metilfenoksi ftalosiyaninato çinko (II) yapısına sahip ftalosiyanin bileşiği PVC membran iyon seçici sensörlerin yapısında aktif madde (iyonofor) olarak kullanıldı. %3 Tetrakis 2-izopropil-5-metilfenoksi ftalosiyaninato çinko (II), %32 PVC, %64 DBF ve %1 KTPClPB bileşimine sahip membran ile hazırlanan sensörün diğer katyonlar yanında Ag^+ iyonuna karşı oldukça seçici olduğu belirlendi. PVC-membran potansiyometrik Ag^+-seçici sensörlerin durgun ortamda sergilediği potansiyometrik performans özellikleri belirlendi. Belirlenen PVC-membran potansiyometrik Ag^+-seçici sensörün durgun ortamda oldukça tekrarlanabilir sonuçlar verdiği gözlendi. Geliştirilen gümüş seçici sensörün analitik uygulaması, sentetik numune analizlerinde başarıyla gerçekleştirildi. Bu çalışmada hazırlanan gümüş- seçici PVC membran potansiyometrik sensör, minyatürize edilebilmesi, ekonomik olması, kolay hazırlanması ve basit kullanım gibi avantajlara da sahiptir. Diğer taraftan geliştirilen sensör Ag^+ iyonlarına karşı yüksek seçicilik gösterdiği için çevresel ve biyolojik numunelerde Ag^+ iyonlarının rutin analizlerinde de kullanılabilir.

Teşekkür

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Bölüm 5

Kuraklık Stresinin Bitkiler Üzerindeki Etkileri ve Tepki Mekanizmaları

Müge TEKER YILDIZ[1]

Giriş

Dünyada tarımsal üretim iklim krizinden ciddi şekilde etkilenir. İklim değişikliği bitki verimini ve gelişimini doğrudan veya dolaylı etkiler olarak sınırlar (El Haddad vd., 2022). Mevcut su, bitkiler de dahil olmak üzere tüm canlı organizmaların yaşamının sürdürülebilirliği için yaşamsal ihtiyaçtır. Özellikle bitkiler fotosentez ve metabolik aktiviteler için suya her daim ihtiyaç duyar. Ancak iklim değişikliğinin negatif sonucu olan kuraklık, bitkinin kullanabileceği toprak suyunu kullanaması ve metabolizmasını olumsuz etkilediği fizyolojik bir su eksikliği olarak tanımlanır (Kumar vd., 2018). Bitkiler kuraklığın neden olduğu negatif etkilere karşı, kendilerini savuma mekanizmaları ile yönetir (Kumar vd., 2018). Kuraklığa verilen tepki mekanizmaların etkileşimi sonucu oluşan fizyolojik ve metabolik değişiklikler, stresin olumsuz etkilerine dayanmaya yardımcı olur.

Bitki stres tepki mekanizmaları, çevresel ve genetik faktörler tarafından belirlenen karmaşık ağlar tarafından kontrol edilir. Farklı savunma mekanizmaları bitkilerin kuraklık stresiyle başa çıkmasına yardımcı olur. Bitki kuraklık stresine biyokimyasal (antioksidan içeriği, klorofil içeriği, prolin birikimi, hormonal, sekonder metabolit vb.), fizyolojik (stoma aktivitesi, fotosentez, ozmotik denge, terleme, yaprak su içeriği) ve morfolojik değişikliklerle (yaprak alanında azalma, yaprak sayısı, kök uzunluğunda artış, yaprak yaşlanması, erken olgunlaşma, büyüme evrelerinde değişiklik vb.) yanıt verir (Nezhadahmadi vd., 2013). Ek olarak, bitkinin stres tepkisi ve başa çıkma mekanizmaları, kuraklık stresi yaşadığı büyüme aşamalarınada bağlıdır. Büyüme aşamalarına bağlı olarak, bitkiler kuraklık stresine daha fazla veya daha az duyarlı olabilir. Vejetatif gelişme döngüsü sırasında kuraklık stresi yaşandığında turgor

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basıncında, yaprak su içeriğinde, stoma hareketlerinde, yaprak renklenmesinde, fotosentez ve solunumda, yaprak canlılığında ve nihayetinde büyüme aktivitelerinde istenmeyen durumlar meydana gelir. Bu tepkiler bitkinin vejetatif dönemini kısa tutmasını ve generatif aşamadan hızla geçmesini teşvik edebilir (Pamungkas ve Farid, 2022). Generatif gelişme döneminde kuraklık stresine maruz kalma çiçeklenme oranında, döllenmede, tohum tutumunda ve ürün kalitesinde azalmalara neden olur (Akram vd., 2019). Birçok araştırmacı kuraklık stresinin sorgum (Sanjari vd., 2021), mısır (Goodarzian vd., 2015) buğday (Mahla vd., 2017), pirinç (Akram vd., 2019), maş fasulyesi (Jincy vd., 2019), soya fasulyesi (Dong vd., 2019) ve mercimekte (El Haddad vd., 2021) etkilerini araştırmıştır. Bununla birlikte, kuraklık stresinin şiddetine ve süresine bağlı olarak bitkinin büyüme dönemi, strese verdiği tepkiyi yönetmede önemli bir faktördür (Çakir vd., 2004).

Bu araştırmada, kuraklık stresinin bitkiler üzerindeki etkileri ve tepki mekanizmaları arasındaki etkileşim hakkında bilgi açıklamayı amaçlamaktadır.

1. Bitkilerde Kuraklık Stresinin Nedenleri

Hava sıcaklığının ve atmosferik CO_2 seviyelerinin sürekli yükselmesi ve bunun da nihayetinde yağış desenlerini ve dağılımını değiştirmesi nedeniyle küresel iklim değişikliğinin gelecekte hızlanması bekleniyor (Yin vd., 2018). Yağıştan kaynaklanan yetersiz su girişi genellikle kuraklık stresinin ana itici gücü olsa da, yüksek sıcaklık olayları, yüksek ışık yoğunluğu ve kuru rüzgar tarafından yönlendirilen buharlaşma yoluyla topraklardan su kaybı, mevcut kuraklık stresi olayını daha da kötüleştirebilir (Cohen vd., 2021). Küresel iklim değişikliği genellikle küresel ölçekte geniş alanlarda yaygın kuraklık stresi koşullarına neden olur. Kuraklığın yanı sıra, tuzluluk stresi de bitkilerde su açığının birincil nedeni olarak kabul edilir (Adnan vd., 2020).

İklim değişikliğinden kaynaklanan hava sıcaklıklarındaki artışlar buzulların erimesine ve düşük veya sıfır eğimli tarım arazilerinin potansiyel su baskınlarına neden olabilir (Cook vd., 2014). Ek olarak, buzulların kaybı su rezervuarlarının küçülmesine neden olarak mahsullerin su teminini sınırlamaktadır ve bu durum zamanla artan bir eğilimdir. Küresel ısınmaya bağlı su kaybı yalnızca toprakta değil, aynı zamanda bitki düzeyinde de meydana gelmektedir. Bitkilerdeki iç su, küresel ısınmadan kaynaklanan artan sıcaklıklar nedeniyle atmosfere büyük ölçüde kaybolmaktadır; bu olgu, dünyanın çeşitli tarımsal sistemlerinde halihazırda var olan su açığı sorunlarını daha da kötüleştirmektedir. Bu yüzyılın sonuna kadar hava sıcaklığındaki beklenen artışların mevcut seviyelerden yaklaşık 2 °C daha fazla olması durumunda, dünya nüfusunun yaklaşık beşte biri ciddi su açığından etkilenecektir (Ray vd., 2019).

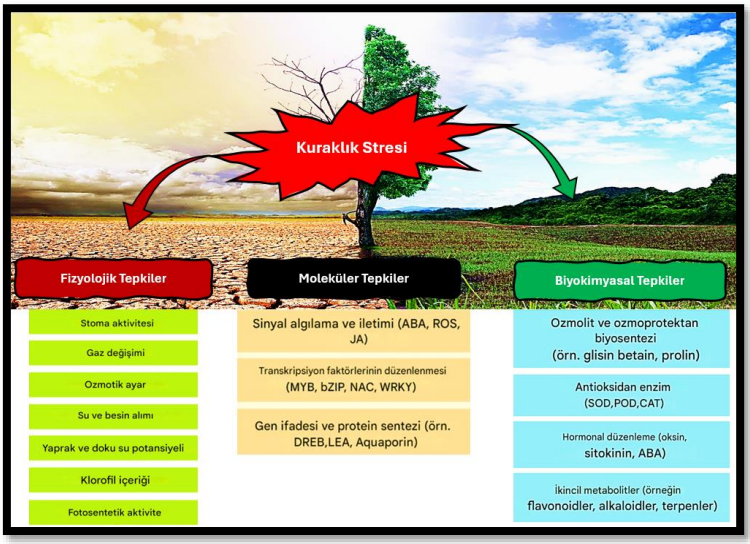
Yaz mevsimi boyunca, muson sistemi dünyanın çeşitli bölgelerinde yağış kaynağı olarak kabul edilir. Tahminlere göre, atmosferdeki CO_2 konsantrasyonundaki doğrusal artış nedeniyle yüksek yağış beklenmektedir ve bu durum ürün üretimini olumsuz etkileyecek ve yoğun nüfuslu ülkelerin tarım sektöründe büyük sellere ve büyük ekonomik kayıplara yol açacaktır (Guo vd., 2015). Bu koşullar altında, muson yağış değişkenliği rizosferin nem seviyesini etkilemektedir ve etkilemeye devam edecektir ve dolayısıyla yağış yoğunluğu, oluşumu ve süresindeki dinamikler yoluyla dünyanın belirli bölgelerinde bitki verimliliğini etkileyecektir.

2. Kuraklık Stresinin Bitkiler Üzerindeki Etkisi

Çevresel koşullardaki dinamiklere bağlı olarak, bitkiler büyümelerini ve gelişmelerini ciddi şekilde etkileyebilecek çeşitli streslerle karşı karşıya kalabilirler. Özellikle tahıl üretimi ve verimi, tarımdaki en sınırlayıcı stres olarak bilinen kuraklık stresinden büyük ölçüde etkilenebilir. Bu nedenle, bitkilerin su kısıtlamasıyla başa çıkma yeteneklerinin araştırılması büyük bir değere sahiptir ve özellikle kurak ve yarı kurak ortamlarda yakın gelecekte de ilgi görmeye devam etmelidir (Sobhanian vd., 2020). Şu anda, maksimum tahıl verimi ve kalitesini hasat etmek için kuraklığa duyarlı mekanizmaları belirlemek amacıyla başlıca temel ürünler yoğun bir şekilde incelenmektedir, ancak gelecekteki çalışmalar ana tahıl ürünlerinin üreme aşamalarında hem ısı hem de kuraklık stresi etkilerinin birleşik etkisine odaklanmalıdır.

Bitkilerin büyümesi ve gelişimi için optimum seviyede su bulunabilirliği gereklidir, optimumun ötesinde toprak nemindeki dalgalanma ürün verimini ve kalitesini etkileyebilir. Öte yandan, rizosferdeki optimumdan daha az su bulunabilirliği bitki büyümesini engeller ve böylece bitki besin alımını engeller (Elemike vd., 2019). İkincisi yakın zamanda ürün üretiminde büyük azalmalardan sorumlu olmuştur ve küresel ısınma ve iklimdeki değişkenlik nedeniyle daha da şiddetli hale gelmesi beklenmektedir (Hafez vd., 2017).

Bitkiler de kuraklık stresi aynı zamanda su kıtlığı, daha az yağış olması veya hiç yağış olmaması nedeniyle oluşur ve bitki savunma mekanizmalarıyla kuraklık stresine tepki verir (Şekil 1). İlk olarak, kökler suyu bulamadığında toprak nem içeriği ve bitkinin yaprak ve gövde gibi hava kısımlarında düşük su potansiyeli oluşur. Bu durum meydana geldiğinde, yapraklardan terleme yoluyla su kaybı oranı, kuru ortamlarda kökler aracılığıyla su alım oranını geçer (Goche vd., 2020). Kökler, genişlemeleriyle daha fazla su almaya çalışır ve bu durum nihayetinde bitkileri su açığı olduğunda stoma kaybını en aza indirmeye adapte eder (Martínez-Vilalta ve Garcia, 2017).



Şekil 1. Bitkilerde kuraklık stresi tepkileri.

Bitkilerdeki kuraklık stresi tepkileri arasında yaprak kıvrılması, yaprakların sararması, yaprakların kavrulması, kalıcı solma yer alır (Corso vd., 2020). Su eksikliğinin bitki performansı üzerindeki olumsuz etkilerine rağmen, bitkiler çeşitli derecelerde su eksikliğine yanıt verme yeteneğine sahiptir (Şekil 1). Bu kuraklık tepkileri fizyolojik, biyokimyasal ve moleküler olarak sınıflandırılmaktadır (Şekil 1).

3. Bitkilerin Kuraklık Stresine Karşı Fizyolojik Tepkileri

Kuraklık stresine dayanmak için hayati önem taşıyan fizyolojik reaksiyonlar terleme yoluyla su kaybını azaltmak için stomaların kısmen kapatılması, uyumlu çözünen maddelerin (ozmoprotektanlar) birikimi yoluyla hücresel turgoru korumak için ozmotik ayarlama, proteinlerin sentezi ve oksidatif stresi dengelemek için antioksidan sistemlerin tetiklenmesi olarak kategorize edilebilir. Aşağıda yukarıda belirtilen diğer tepki sınıflandırması ayrıntılı olarak açıklanmaktadır.

3.1. Stoma Tepkileri ve Gaz Değişimi

Stoma kapanması, bitkilerin terlemeyi azaltmak ve kuraklık stresiyle başa çıkmak için kullandıkları önemli bir mekanizmadır. Stomalar, fotosentez için CO_2 alımı ve oksijen salınımı dahil olmak üzere gaz değişimini düzenler . Stoma kapanması, bitkilerde su eksikliği koşullarının başlangıcına karşı yaygın bir adaptif tepkidir. Bitkiler, su eksikliğine epidermal iletkenliğin azalması ve stoma

kapanması yoluyla su kaybını sınırlayarak yanıt verirler (Harb vd., 2010). Stoma kapanmasıyla örneklenen susuz kalma önleme stratejisi, yapraklardan su kaybını azaltır. Ancak, bu eylem aynı zamanda CO_2 alımını kısıtlar , reaktif oksijen türleri (ROT) üretir, fotosistem II'ye (PSII) zarar verir ve fotosentezi engeller, sonuç olarak ürün verimini azaltır. Stoma kapanmasını indükleyen ABA fitohormonunun sentezlenmesi ve harekete geçirilmesiyle desteklenir. Stoma kapanması hem pasif hem de aktif (ABA aracılı) mekanizmalar tarafından yönlendirilir. Bu kapanma, terleme yoluyla su kaybını azaltarak bitkinin kuraklık stresi sırasında suyu korumasına yardımcı olur (Agurla vd., 20218). Kuraklık toleransını artıran bir süreç olan kuraklık ön hazırlığı, stoma davranışını kuraklık stresine yanıt olarak iyileştirmiştir. Kuraklık ön hazırlığının hem stoma kapanmasını hem de yeniden açılma oranlarını iyileştirerek kuraklık toleransını artırdığı bulunmuştur. Stoma kapanma sürecinin bu önemli noktası, bitki türüne ve kuraklık stresinin meydana geldiği koşullara bağlıdır (Yang vd., 2023). Bu nedenle, stoma kapanmasının düzenlenmesi, bitki stres dayanıklılığının ve uygunluğunun hayati bir bileşenidir ve bitkilerin su kaybını en aza indirmesini ve kuraklık koşullarıyla başa çıkmasını sağlar. Su stresi sırasında, bitki stomaları suyu korumak için kapanır, bu da yaprak yüzeyinden su buharı kaybını azaltır ve terleme oranlarını düşürür. Bu adaptif yanıt, fotosentezde bir azalmaya, yaprak düzeyinde daha büyük bir içsel su kullanım verimliliğine ve CO_2 alımında bir azalmaya yol açar. Stoma kapanması, terleme bitkinin soğumasına yardımcı olduğu için yaprak sıcaklık düzenleme mekanizmasını etkileyebilir. Azalmış terleme, bitki metabolizmasını etkileyen yüksek yaprak sıcaklıklarına yol açar. Araştırmalar, kuraklık stresi sırasında stoma iletkenliğinin azalmasının fotosentezi azalttığını ve daha kuru koşullara maruz kalan bitkilerin su kullanımını optimize etmek için stoma özelliklerini değiştirdiğini ve bunun da su kullanım verimliliğinin artmasına yol açtığını göstermiştir (Driesen vd., 2023).

Stoma kapanması CO_2 girişini sınırlar ve bu da fotosentez oranında düşüşe yol açar; bu da genel bitki büyümesini ve üretkenliğini etkileyebilir. Su stresi altındaki bu stoma kapanması iletkenliği de azaltır ve bu da fotosentez oranında düşüşe ve yaprak düzeyinde daha yüksek bir içsel su kullanım etkinliğine yol açar. Bu adaptif yanıt bitkilerin suyu korumasına yardımcı olsa da, fotosentez ve genel üretkenlik açısından dezavantajları vardır. Sonuç olarak, kuraklık stresi sırasında stomaların kapanması bitki fizyolojisini etkiler ve fotosentez aktivitesi ile su tasarrufu arasındaki karmaşık dengeyi vurgular (Joshi vd., 2022).

Stoma kapanması, ABA gibi hormonal sinyaller de dahil olmak üzere karmaşık sinyal yolları tarafından düzenlenir ve bitkinin su durumu ve atmosferik nem gibi çevresel faktörlerden etkilenir. Su eksikliğinde stoma durumunun düzenlenmesi, esas olarak, yaprakta birikmesi stoma kapanmasını aktive eden

ABA tarafından aracılık edilir (Tombesi vd., 2015). Sitosolik pH, ROT, NO ve serbest Ca^{2+}, stoma kapanmasında rol oynayan diğer sinyal molekülüdür (Agurla vd., 2018). ROT tepkilerindeki ve stoma kapanmasındaki farklılıklar kuraklığa adaptasyonlarını etkilemiştir. Dahası, stoma aktivitesinin kuraklık toleransı ile güçlü bir şekilde ilişkili olduğu iyi belgelenmiştir. Ancak, stoma morfolojisi ve yoğunluğundaki değişikliklerin mahsulün kuraklığa toleransını nasıl etkilediğine dair sınırlı araştırma vardır. Stoma yoğunluğunun değiştirilmesinin, besin alımını olumsuz etkilemeden kuraklık toleransını artırdığı gösterilmiştir (Bertolino vd., 2019). Ayrıca, Lonbani ve Arzani (2011), kuraklığa dayanıklı tritikale çeşitlerinin diğer tritikale ve buğday çeşitleriyle karşılaştırıldığında daha az stoma sayısına sahip olduğunu göstermiştir. Stoma sayısı ve hareketi de dahil olmak tüm gaz değişimi bitkilerin fizyolojik tepkilerinde önem arz etmektedir.

3.2. Ozmotik Ayarlama

Ozmotik ayarlama, su kaybını önleyerek ve hücre dinamikliğini koruyarak bitkilerin kuraklık gibi zorlu çevre koşullarında hayatta kalmasını ve gelişmesini sağlayan kritik bir tepki mekanizmasıdır. Kuraklığa dayanıklı genotipler, hücre turgorunu korumaya yardımcı olan ozmotik ayarlama yoluyla su kıtlığına karşı direnç gösterir (Khan vd., 2018). Su eksikliklerine yanıt olarak temel adaptif mekanizmalardan biri, hücrelerde çözünen maddelerin birikmesidir. Kanıtlar, ozmotik ayarlamanın kuraklığa eğilimli ortamlarda yetiştirilen tarımsal bitkilerin verimi artırdığını göstermektedir (Turner, 20218). Vakuollerde çözünen maddelerin birikmesi, sitozolik çözünen maddeleri tamponlamaya ve metabolizmayı desteklemeye yardımcı olan geri dönüşümlü bir fizyolojik süreçtir. Bitkiler turgoru öncelikle çözünen maddeleri biriktirerek ve potansiyel olarak hücre zarlarının elastik ayarlaması yoluyla düzenleyebilir. Diğer yandan, Prolin, çeşitli şekerler ve glisin betain gibi uyumlu çözünenleri sentezlemek için genlerin ifadesi ile hücrede birikmi artarak, ozmotik ayarlamayı düzenler. Bir çok çalışma, ozmotik ayarlamanın ve hücrelerde susuzluğa toleransta uyumlu çözünen maddelerin birikiminin rolünü inceleyerek, bitkilerde su stresi altında üretimi desteklemede ozmotik ayarlamanın önemini vurguladı (Blum, 2017).

3.3. Ozmolitlerin Birikimi

Bitkiler su eksikliği koşulları ve susuzluk riski yaşadıklarında, hücresel turgor basıncı azalır ve bu da fizyolojik süreçleri olumsuz etkiler. Bitkiler, ozmotik ayarlama stratejileri kullanarak hücre turgorunu korumayı ve kuraklık koşullarında solmayı önlemeyi amaçlar (Oguz vd., 2022). Hafif kuraklık altında, kuraklığa dayanıklı genotipler, uyumlu çözünen maddeleri biriktirerek ve önemli fizyolojik aktiviteleri sürdürerek ozmotik basıncı ayarlayarak buharlaşmalı su

kaybını azaltır (Harb vd., 2010). Vakuollerde çözünen maddelerin birikimi de kuraklık toleransını önemli ölçüde etkiler. Bu nedenle, sitozolik veziküller ve vakuoller dahil olmak üzere, uyumlu çözünen maddeler hücrelerin içinde biriktiğinde, bitkilerin şiddetli susuzluğa dayanmasına ve su eksikliği koşullarında hücresel turgoru korumasına yardımcı olmak için çok önemli olan ozmotik ayarlamayı kolaylaştırırlar.

Prolin, bitki hücrelerinin ve proteinlerinin yapılarını stabilize etmeye yardımcı olur ve ayrıca ROT temizlemede görev alır. Dehidratasyon koşulları altında prolin, biyosentezinin yukarı düzenlenmesi ve bozunmasının inhibisyonu nedeniyle birikir. Prolin, glutamik asitten türetilen bir amino asittir. Prolin birikimi genellikle stres toleransı ile ilişkilidir; burada strese dayanıklı bitki genotiplerinde, strese duyarlı bitki genotiplerine göre daha yüksek birikimler meydana gelir (El Moukhtari vd., 2020). Prolinin ekzojen uygulaması, kuraklık stresinin mahsul bitkilerinin büyümesi ve verimliliği üzerindeki olumsuz etkilerini hafifletir (El Moukhtari vd., 2020). Prolin, kuraklık ve tuzluluk gibi abiyotik stresi hafifletmeye yardımcı olurken, özellikle kuraklık stresi koşullarında rolü daha da önem kazanır.

Glisin betain (GB) ve β-alanin betain (AB), hücresel çözünen maddeler olarak görev yapan diğer dördüncül amino asit türevleridir (Chun vd., 2018). Benzer şekilde, bu ozmoprotektanlar hücresel yapıları ve proteinleri stabilize etmede ve hücreleri ROT temizleme yoluyla oksidatif hasardan korumada rol oynar. Glisin betain genellikle kuraklık stresi koşulları altında bitkilerde birikir.

Şekerler Şeker birikimi kuraklık tarafından sürekli olarak tetiklenir ve bitkilerdeki kaynak-havuz ilişkisini değiştirir (Kaur vd., 2021). Bitkiler, hücresel ozmotik ayarlamaya katkıda bulunan ve stres dönemlerinde enerji kaynağı görevi gören sakaroz, glikoz, galaktoz, maltoz, laktoz, rafinoz ve fruktoz gibi şekerleri biriktirir (Ghosh vd., 2021). Şekerler, ozmotik potansiyeli ayarlamak için ozmolit görevi görür ve bitkilerde ozmoprotektan görevi görür Şekerler, poliaminler ve diğer uyumlu çözünen maddeler gibi ozmolitlerin birikimi, su eksikliği stres koşulları altında hücresel yapıları korumada rol oynar. Şekerlerin dışarıdan uygulanması, bitkilerin büyümesi ve gelişimi üzerindeki su stresinin olumsuz etkilerini hafifleterek kuraklığa dayanıklılığı da artırır (Ahmad vd., 2020).

Polioller Mannitol, inositol, galaktinol, eritritol, gliserol, pinitol ve sorbitol dahil olmak üzere polioller veya şeker alkolleri, kuraklık stresine yanıt olarak daha yüksek bitki hücrelerinde birikebilir. Polioller, kuraklık stresi koşulları altında bitki hücrelerinin ozmotik ayarlanmasında uyumlu çözünen maddeler olarak önemli bir rol oynar (Gugliuzza vd., 2020). Bu çözünen maddelerin birikimi hücresel ozmotik potansiyeli hafifletir, turgor basıncını korur ve sınırlı su bulunabilirliği koşullarında temel hücresel işlevleri sürdürür.

3.4. Antioksidan Savunma Sistemleri

Antioksidan sisteminin aktive edilmesi, yüksek bitkilerin kuraklığın ikincil etkilerinden kaynaklanan oksidatif strese karşı koymak için kullandıkları önemli bir mekanizmadır (Kouighat vd., 2024). Oksijen toksisitesinin bitki hücreleri üzerindeki geniş kapsamlı etkileri nedeniyle, oksidatif stres pro-oksidanlar ve antioksidanlar arasındaki dengede bir kayma ile karakterize edilir, pro-oksidanları destekler ve potansiyel hasara yol açar. ROS terimi hem serbest radikalleri hem de bunların radikal olmayan ara maddelerini ifade eder. Bir veya daha fazla eşleşmemiş elektron içeren türlere serbest radikaller denir ve bu eksik elektron kabuğu onlara yüksek reaktivite kazandırır. Biyolojik sistemlerde, serbest radikaller azot ve oksijenden üretilebilir. Su eksikliği sırasında, pro-oksidanlar ve antioksidanlar arasındaki denge bozulur ve bitki hücrelerinde reaktif azot türleri (RNS) ve ROT birikir. Süperoksit radikalleri, hidroksil radikalleri ve hidrojen peroksit gibi ROT'lar, peroksinitrit ve nitrik oksit gibi RNS'lerle birlikte proteinler, lipitler ve nükleik asitler gibi biyomolekülleri oksitleyerek hücresel zarara neden olma potansiyeline sahiptir (Huang vd., 2019). Bitkiler, oksidatif stresin zararlı etkilerini azaltmak için karmaşık antioksidan savunma sistemleri geliştirmiştir. Antioksidan savunma sistemi, ROS detoksifikasyonu, zarlardaki lipid peroksidasyonunun azalması ve oksidasyonu geciktirerek ve nükleik asit (DNA) hasarını onararak proteinlere verilen hasarı engelleme yoluyla oksidatif strese karşı yeterli koruma sağlar (Fujita vd., 2022). Antioksidan sistem iki bölüme ayrılabilir: enzimatik olmayan ve enzimatik. RNS ve ROT'u temizlemedeki rolleriyle bilinen enzimatik antioksidanlar katalaz (CAT), süperoksit dismutaz (SOD), glutatyon peroksidaz (GPX), peroksidaz (POX), glutatyon redüktaz (GR) ve glutatyon-S-transferaz (GST) ve askorbat peroksidaz (APX) olarak adlandırılabilir (Rajput vd., 2021). AsA-GSH döngüsü, glutatyon (GSH) ve askorbik asit (AsA) gibi enzimatik olmayan antioksidanları da kullanarak hidrojen peroksidi (H_2O_2) detoksifiye etmek için kullanılan bitki hücrelerinde önemli bir antioksidan savunma yoludur (Hasanuzzaman vd., 2020).

Araştırmalar kuraklığa dayanıklı genotiplerin antioksidan savunma sistemlerinde farklı aktivite gösterdiğini, kuraklığa duyarlı olanlarla karşılaştırıldığında daha düşük ROT birikimine ve süperoksit dismutaz (SOD), peroksidaz (POD), katalaz (CAT) gibi antioksidan enzimlerin daha yüksek miktarına yol açtığını göstermiştir (Wang vd., 2019). Ek olarak, geriye doğru sinyalleme yoluyla antioksidan aktivitenin yukarı düzenlenmesi, bitkilerin oksidatif strese alışmasında önemli bir süreçtir ve belirli bitki türlerinin artan kuraklık toleransına katkıda bulunur. Dahası, kuraklık stresini hafifletmede ekzojen düşük doz hidrojen peroksitin rolü ve canlanma bitkilerinde koruyucu

makinenin aktivasyonu da bitkilerdeki antioksidan aktivite ve kuraklığa tolerans bağlamında incelenmiştir.

4. Bitkilerin Kuraklık Stresine Karşı Moleküler Tepkiler

Bitkisel ürünlerde kuraklık toleransını artırmak, altta yatan moleküler mekanizmaların iyice anlaşılmasını gerektirir (Ebrahimi vd., 2021). Bir çok sinyal iletim molekülleri gen aktiviteleri ifadesinde genetik ve epigenetik değişiklikleri tetikleyerek nihayetinde toleransın gelişmesine yol açabilir. Bu işlevsel ve moleküler mekanizmaları daha ayrıntılı olarak keşfetmek, bitki kuraklık toleransını güçlendirmeye yönelik etkili üreme stratejileri geliştirmek için önemlidir. Kuraklık stresine dayanıklıkta moleküler tepkiler; sinyalleme genlerinin indüksiyonu, transkripsiyon faktörlerinin indüksiyonu ve strese yanıt veren genlerin indüksiyonu sayabiliriz (Şekil 1).

Bu düzenleme seviyeleri paraleldir ve birbirleriyle etkileşime girerek, büyük olasılıkla entegre bir gen ağı aracılığıyla bitkinin zorlu çevre koşullarına uyum sağlamasına ve hayatta kalmasına yol açar.

5. Bitkilerin Tarımsal Sürdürülebilirliği İçin Gelecekteki Araştırma Kapsamı

Dünya nüfusunun artan gıda talebini karşılamak için tarımsal üretimde abiyotik streslerden kaynaklanan verim kayıplarının önlenmesi hayati önem taşımaktadır. Bitki stres toleransını artırmanın ön koşulu, bitkinin strese verdiği tepki mekanizmalarının anlaşılmasıdır. Abiyotik strese toleransı artırmada yenilikçi ve biyoteknolojik yöntemler büyük önem taşımaktadır (Hossain vd., 2021). Bu bağlamda, araştırmacılar bitki stres toleransını geliştirmek için farklı omik yaklaşımlar kullanmaktadır. Küresel olarak ve özellikle kurak ve yarı kurak ortamlarda, bitkiler kaçınılmaz olarak su kıtlığıyla karşı karşıya kalır ve bu da büyümeleri ve genel üretkenlikleri için önemli bir tehdit oluşturur. Özellikle yarı kurak ve kurak ortamlarda bitkilerin su kıtlığına adaptasyonuyla ilgili zorluklar ve gelecekteki yönler hakkında içgörüler sağlar.

Yerel popülasyonlar, geniş genetik çeşitliliği nedeniyle kuraklık stresine dayanıklı bitki ıslahı ve seleksiyon çalışmalarında kullanılması gereken önemli kaynaklardır (Karavidas vd., 2022). Özellikle kuraklığa dayanıklı çeşit ıslahında kullanılan yerel bitki popülasyonlarının agronomik bitki özellikleri ve stres koşulları altındaki performansları dikkate alınmalıdır. Çünkü tarla bitkilerinde verim, bitki boyu, başak sayısı, tane ağırlığı, hasat indeksi, bin tane ağırlığı ve tane verimi gibi bazı agronomik bitki özelliklerine bağlıdır (Sabella vd., 2020).

Son yıllarda araştırmacılar, çevre dostu yenilikçi yaklaşımlarla bitkilerdeki verim kayıplarını önlemeye odaklanmışlardır. Değişen iklim koşullarında ve

abiyotik stres faktörleri altında, biyo-gübrelerin, biyo-uyarıcıların ve tarımsal-endüstriyel atıkların kompost olarak kullanılması sürdürülebilir tarım için önemlidir (Boutasknit vd., 2020). Bu yaklaşımların tarımsal sürdürülebilik için hayati önem taşıması nedeniyle saha denemeleriyle desteklenmesi gerekir. Ayrıca farklı iklim koşullarında saha denemeleri yapılması literatürü desteklemeye önemli katkı sağlayacaktır.

6. Sonuçlar

Küresel iklim değişikliği nedeniyle bugün olduğu gibi gelecekte de kuraklığın bitkisel üretimi kısıtlayan birincil faktör olacağı açıktır. Kuraklık stresi bitki büyümesini ve verimi etkiler. Stresin zamanlaması, süresi, şiddeti ve hızı şüphesiz bir bitkinin su eksikliğine verdiği tepkiyi belirlemede önemli bir rol oynar. Ancak kuraklık doğal koşullar altında kontrol edilmesi zor bir durumdur. Bitkilerin farklı büyüme evrelerinde strese verdiği tepki, yüksek stres toleransına sahip çeşitlerin geliştirilmesi için önemli bir ölçüttür. Bitkilerin strese verdiği tepki, moleküler, biyokimyasal, fizyolojik ve morfolojik mekanizmaların işbirliği sonucu ortaya çıkar. Bu mekanizmaların her biri ayrı ayrı ele alınamayacak kadar karmaşıktır. Bitkinin önemli gelişme evrelerinde bu mekanizmaların aktivasyonu ve düzenlenmesindeki farklılıklara odaklanmak yeni yaklaşımlara yol açabilir. Bu derlemede kritik vejetatif ve generatif dönemlerde kuraklık stresine verilen tepkiyi açıklamaya çalıştık. Sonuç olarak kuraklığın kritik büyüme evreleri üzerindeki etkisinin belirlenmesi, verim kayıplarının önlenmesi için yapılacak çalışmalara rehberlik edecektir.

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