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INTERNATIONAL STUDIES
in
SCIENCE AND MATHEMATICS

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Chapter 1

INTERSTELLAR MEDIUM AND STAR FORMATION

E.Nihal ERCAN[1]

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There are an estimated 100 billion stars in our galaxy, the Milky Way, only. The formation of those stars has been one of the popular interests in astronomy for decades. As esteemed Astronomer Jocelyn Bell Burnell once said, “There is stardust in your veins. We are literally, ultimately, children of the stars.” So, we humans are simply looking for our origins, after all.

Humans have always been curious about the stars. In ancient times, stars were used for navigation and timekeeping and were also woven into many myths and stories. Babylonians even made a star catalogue based on their observations for farming purposes (Rogers, J. H., 1998), but our “scientific” quest for stars only started in the past few centuries with the invention of modern instruments.

The first stars in our Universe are believed to form 200-400 hundred million years after the Big Bang, approximately 13.7 billion years ago. Although we now have modern, powerful telescopes like Spitzer, Hubble, Chandra, Keck and ALMA, it is not known exactly what the first stars looked like. Also called “Population III” stars, the first stars have been made of hydrogen and helium only, for these are the elements formed directly after the Big Bang. (*What Were the First Stars Like?*, n.d.)

The interstellar medium (ISM) is the matter and radiation found between the star systems, mainly gas and dust. Helium and hydrogen are the main elements in the ISM (about 98% of its mass). Carbon, oxygen and other metals make up the remaining 2% of its mass, generally in gas form but some heavier elements form dust. ISM serves as the raw material for star formation; thus, studying it is crucial for understanding stars’ life cycle and galaxies’ structure (*Interstellar Medium and Molecular Clouds, Harvard & Smithsonian*, 2024).

In this article, we will examine star formation deeply and explain the role of the interstellar medium based on observational and theoretical data.

Observational Aspects of Star Formation

Observational astronomy is extremely essential for understanding how stars form and to better grasp the idea of the interstellar medium (ISM). Astronomers collect serious data by systematically observing celestial objects over numerous wavelengths to help prove and clarify theoretical models. Results from data collected through different telescopes around the world are used as an aid for identifying the *molecular clouds* aka *stellar nurseries*, which ,as the name implies, are the primary birthplace for new stars.

Imaging, spectroscopy and radio astronomy are some of the techniques that astronomers use to examine composition, temperature and behaviour of the ISM, offering us a better understanding of the conditions which support or prevent the collapse of dust and gas into new stars. Moreover; as the technology improved, more powerful instruments were added to the collection, which overall enhanced our ability to identify faint and isolated star-forming regions concealed by interstellar dust. I think it is quite fair to say that instruments like ALMA (Atacama Large Millimeter Array), Hubble Space Telescope, and James Webb Telescope, which in only two years following its launch has delivered groundbreaking details that shed some light on the formation of new stars[1], are revolutionary in a sense that they extended our vision by providing high resolution and detailed spectral data.

Tools and Techniques Used for Understanding Star Formation

Radio Telescopes:

These telescopes are used to detect radio waves and microwaves emitted by celestial objects, covering wavelengths between roughly 10 meters and 1 millimeter.

They are quite helpful for examining molecular lines (e.g., CO emission) to study stellar nurseries.

Optical Telescopes:

These are designed to collect and focus light primarily from the visible spectrum of electromagnetic waves, enabling magnified visual observation, photography, or data collection.

They are in use for discovering and charting nebulae and star clusters.

- Infrared telescopes detect celestial objects by using infrared light.

Infrared Telescopes:

Currently, these telescopes are used to observe protostars and young stars by looking through dust clouds, like Spitzer and James Webb Space Telescopes!

Space-Based Observatories:

Also called space telescopes, these are located in outer space to observe astronomical objects.

---

[1] Webb has discovered ice and numerous complex organic molecules in the clouds where stars begin to accumulate mass, offering new information about their patterns of consuming and expelling material. (*Webb's Star Formation Discoveries*, n.d.)

Out of atmosphere, out of distortions, thus resulting in better resolution and clearer images—like Hubble and James Webb Space Telescopes!

Here is an example of the Orion Nebula which is a well-known star-forming region. This image reveals how newly formed stars shape the surrounding gas and dust:

Figure 1. Credit: NASA, ESA, M. Robberto (Space Telescope Science Institute/ ESA) and the Hubble Space Telescope Orion Treasury Project Team)

Major Observational Discoveries

Molecular Clouds (Stellar Nurseries):

The discovery of molecular clouds are closely linked to the progress in radio astronomy and also, astrochemistry. Two physicists, Ewen and Purcell detected the 21 cm hydrogen emission line in 1951 which essentially helped astronomers map the Milky Way. The search for interstellar molecule continued with OH in 1963 and NH_3 in 1968. Yet, detecting molecular Hydrogen, which is the most abundant one, yielded no results for a while because of its weak emissions. Finally in 1970, Arno Penzias, Keith Jefferts and Robert Wilson found CO in the **Sagittarius B2** cloud, making it the first identified *molecular cloud.* It is then confirmed that **CO** is a more *effective* tracer for star formation.

Interstellar Medium:

In 1904, Johannes Hartmann made a revolutionary discovery, the interstellar medium, using the Potsdam great refractor. He observed stationary Calcium H and K lines in the spectrograms of δ Orionis, a binary star in Orion's Belt. This practically showed that there is a gas between the stars, other than the motion of the binary system. His work was the first to recognize such a concept as a significant part of space.

Protostellar Objects:

A *protostar* is an early stage star that still accumulates mass from its parent molecular cloud which makes it the initial phase in the stellar evolution. The first protostars were identified in the 1960s and 70s when astronomers discovered young stars within dark clouds during infrared surveys, hiding from eyesight. These stars were different from pre-main sequence (PMS) stars because their brightness was higher due to their energy from accretion. This marked the first (observational) proof of the earliest stage in the star formation. Thanks to these discoveries, we are now using advanced infrared telescopes (like James Webb) to search for protostars and study their evolution along the way.

Other than these, one can provide some information about Star Formation Rates (SFR). SFR is a very important parameter used in astrophysics, especially for star formation. It is basically a measurement of the total mass of stars formed yearly (Fuchs, 2014) and is crucial for understanding galaxy evolution, the distribution of stars, and the interaction between the ISM and stars (Kennicutt & Evans, 2012).

There are numerous methods for measuring SFR, some of them are as follows:

Hα Emission, directly linked to young and massive stars

UV Continuum, useful for newly formed stars

IR Emission, good for hidden star formations

Radio Continuum Emission, this one is not affected by dust so best for the study of hidden regions

Far- Infrared Observations, good for the initial stages of star formation

Now that we fully acknowledge how *vital* the observations are for star formation, let us move on to the theoretical aspect of this phenomenon.

Observational data by itself is almost never enough to explain complex concepts in astrophysics. Thus, theories help us context-wise, explaining *why* certain things are observed and *what* to expect in different situations. There are complicated interactions between gas, dust, radiation and magnetic fields when it comes to interstellar medium and star formation; using theoretical models helps clarify these interactions, uncovering mechanisms that cannot be directly observed. (McKee & Ostriker, 2007)

Theories of Star Formation

In this part of the chapter, we will provide brief information on *Gravitational Collapse, Accretion Disk Formation*, and *Feedback Mechanisms.*

Gravitational Collapse:

Gravitational collapse is the primary mechanism that starts star formation. A molecular cloud starts contracting under its own gravity until nuclear fusion begins in its core and boom! A new star is born! Just like a wise professor once said, Gravity always wins!

Jeans Instability

Sir James Jeans introduced the concept of Jeans instability in 1902. This concept explains when an interstellar gas becomes unstable due to gravity and starts collapsing (Jeans, 1902). The Jeans criterion measures the balance between a cloud's thermal pressure and gravitational pull.

Jeans Mass

$$M = \left(\frac{5kT}{G\mu m_H}\right)^{3/2} \left(\frac{3}{4\pi\rho}\right)^{1/2}$$

k : Boltzmann constant

T : Temperature of the cloud

G : Gravitational constant

μ : Mean molecular weight

m_H: Mass of a hydrogen atom

ρ : Density of the cloud

(Credit: Michael Richmond

Conditions for Collapse:

Mass Criterion: A cloud collapses when its mass exceeds M (Jeans mass), as gravity becomes stronger than internal pressure.

Density and Temperature: Cloud is more likely to collapse when the temperature is low and the density is high.

Additionally, Jean's Criterion has a counterpart in observational data. When observed, molecular clouds frequently show regions where the criterion is satisfied or surpassed. This supports the theory that gravitational collapse acts as the *main* mechanism in star formation (Jeans, 1902; Larson,1981).

Accretion Disk Formation:

When a molecular cloud collapses under gravity, conservation of angular momentum results in the formation of an accretion disk around the emerging protostar. This disk is essential for accumulating mass and, finally, for the formation of planetary systems. Composed of gas and dust that spiral inward toward the star, the disk progressively moves mass and momentum outward.

This whole accretion process plays a role in the protostar's luminosity and temperature. Also, the angular momentum of the disk affects the forming star's rotation speed.

There is, again, a counterpart of this phenomenon in the observational field. Telescopes like ALMA and Hubble Space Telescope, which have high resolution, showed plenty of protostellar disks in their images. Furthermore, in the spectroscopic studies, emission lines detected in disks provide evidence for continuing accretion and material flow. (Shu et al., 1987)

Feedback Mechanisms:

Newly formed stars affect the interstellar medium surrounding them which regulates the future star formation and influences the galaxy's structure. This whole process is called the *feedback mechanism.*

Stellar Winds are the continuous flow of ionized gas from a star's outer layers, specifically massive ones. They can create bubbles or cavities in the interstellar medium by removing gas and dust; that change in the surroundings can generate gravitational collapse nearby and thus cause star formation. (Elmegreen & Scalo, 2004)

Radiation from massive stars applies pressure to the nearby dust and gas. If it is powerful, it can ionize and break apart molecular clouds, resulting in star formation.

Supernovae are violent explosions at the end of a star's life (a massive one). The shockwaves created by these explosions can cause disruption in the surrounding ISM, triggering the collapse of a nearby cloud and eventually contributing to star formation (Positive feedback).

Once again, observational data has a counterpart. Studying the interaction between supernova remnants and molecular clouds helps uncover their role in shaping the *ISM* and influencing *star formation*.

Phases of Interstellar Medium

This section will be about the phases of ISM, which are *Cold Neutral Medium (CNM)*, *Warm Neutral Medium (WNM)*, *Warm Ionized Medium (WIM)* and *Hot Ionized Medium (HIM)*

Cold Neutral Medium (CNM):

Temperature is approximately 50-100 K

Primarily composed of neutral Hydrogen and molecular Hydrogen.

It serves as the *primary reservoir* for stellar nurseries

The gravitational collapse in dense areas of this medium triggers star formation.

Warm Neutral Medium (WNM):

Temperature is around 6000-10000 K

Composition is mostly neutral Hydrogen

This medium serves as a transitional layer between CNM and HIM

Warm Ionized Medium (WIM):

Temperature is around 6000-10000 K

Composition is ionized Hydrogen and other ions

This medium spreads through large areas of the ISM, helping with ionisation and linking different ISM phases

Hot Ionized Medium (HIM):

Temperature is around 1-10 million K

Composed of highly ionized Hydrogen and heavy elements

This medium is mainly created by supernova explosions and stellar winds (from massive stars).

They supply energy to the ISM, causing turbulence while sustaining the multiphase structure. They also drive galactic winds that can remove gas and metals, shaping the galaxy's evolution.

Figure 2. Credit: NASA, ESA, K. Stapelfeldt (NASA JPL), G. Kober (NASA/ Catholic University of America)

Discussion and Conclusions

Throughout this study, we explored the processes of star formation and characteristics of the ISM intricately by examining both observational and theoretical aspects of the phenomenon.

e mentioned that the highlights were the vital role of observational astronomy for a better understanding of star formation. We mentioned optical instruments used for observations, like Hubble and James Webb Space Telescopes. Using modern instruments, astronomers can identify and study stellar nurseries and protostars, and they can also measure star formation rates for different regions in space. Some key discoveries mentioned were the detection of ISMs, stellar nurseries and early-stage *protostars*, all of which are the fundamental properties for star formation.

Also, we criticized theoretical models such as *gravitational collapse* and *Jeans instability,* which give us the necessary information on *how* a molecular cloud collapses and forms a star. Then, the *formation of accretion disks* around protostellar objects was discussed for how important it is regarding the mass accumulation and also for planetary systems. Moreover, *feedback mechanisms* that include *stellar winds, radiation* and *supernova explosions* were discussed in this chapter, pointing out the importance of each of their roles in star formation and maintaining the balance of interstellar medium. Lastly, we covered the topic *phases of the ISM*, addressing their distinct properties and *how* they contribute to the formation of stars.

When we combine the insights from observational data and theoretical models, it is clear that these two provide us with an enhanced and comprehensive understanding of star formation and the interstellar medium. The study of star formation is a complex and dynamic field that integrates both observational and theoretical aspects. The multi-phase structure of the ISM is indispensable for controlling the formation processes, exposing how various parts of the ISM work together to support or prevent star formation.

When supported with high-end technology telescopes, research in the future will further untangle the mysteries of our Universe and will help us better understand the complexity of star formation. But until then, here is a star being born that is captured by the Hubble Space Telescope.

I would like to thank Esma Kerkez, one of my undergraduate students, for her help in preparing the manuscript.

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Chapter 2

SOME RESULTS ON NUMERICAL RADIUS OF HARDY-STEKLOV TYPE OPERATORS

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1. Introduction

The inner product norm $(\cdot,\cdot)$ in a complex Hilbert space, $\mathfrak{H}$, induces the norm $\|\cdot\|$. The Banach algebra of bounded linear operators acting on $\mathfrak{H}$ is denoted by $B(\mathfrak{H})$, and its operator norm is defined like this:

$$\|\mathfrak{B}\| = \sup_{\|x\|=1}\{\|\mathfrak{B}x\|:\ x \in \mathfrak{H}\}, \mathfrak{B} \in B(\mathfrak{H}).$$

The image of the sphere of $\mathfrak{H}$ under the quadratic form $x \to (\mathfrak{B}x, x)$ connected to a bounded linear operator $\mathfrak{B}$ on $\mathfrak{H}$ is the numerical range $W(\mathfrak{B})$. To be more specific,

$$W(\mathfrak{B}) = \{(\mathfrak{B}x, x): x \in \mathfrak{H},\ \ \|x\| = 1\}$$

is the numerical range for a $\mathfrak{B}$ on $\mathfrak{H}$. This range is the image of the unit sphere of $\mathfrak{H}$ under the quadratic form $x \to (\mathfrak{B}x, x)$ connected to the operator.

It is commonly known that an operator's spectrum is contained in the closure of its numerical range and that its numerical range is convex (the Toeplitz-Hausdorf theorem). If and only if $W(\mathfrak{B}) \subset \mathbb{R}$, then $\mathfrak{B}$ is a self-adjoint. The following inequalities and

$$w(\mathfrak{B}) = \sup\{|\gamma|:\ \gamma \in W(\mathfrak{B})\}$$

define the numerical radius of an operator $\mathfrak{B}$. It contends that

$$\frac{\|\mathfrak{B}\|}{2} \leq w(\mathfrak{B}) \leq \|\mathfrak{B}\|$$

(see [1]).

The more detail information of numerical range and numerical radius it can be found in [1-3].

In [4-8], the continuity properties of Davis-Wielandt radius and Davis-Wielandt Crawford numbers functions, ratio Crawford number functions, Berezin number function and p-numerical radius function have been investigated.

In [9-11], some convergence properties of p-numerical radii, p-Crawford numbers sequences, (p,q)-numerical radii, (p,q)-Crawford numbers sequences and some spectral characteristics of the converging operator sequences have been investigated.

In [12], some estimates have been obtained by means of the number of differences between the operator norm of the analytic functions of the linear bounded Hilbert space operator and the numerical radius.

In [13], some estimates of this value were obtained using the difference numbers of powers of the associated Hilbert space operators.

In [14-16], some spectral characteristic numbers of direct sum of operators and the gaps between them have been investigated.

Operators related to the compatible gaps of coordinate operators have been identified in [17] by comparing the gaps between operator norm and the spectral and numerical radii of the tensor.

In [18-20], relationship between operator norm and spectral radius of the anti-diagonal block operators matris, upper triangular double bond black operator infinite matrices and nxn block operator matrices in the direct sum of appropriate spaces have been explored.

In the present study, some questions about of numerical radius function of following Hardy-Steklov type operator

$$H_\varphi f(x) = \int_0^x \varphi(t)f(t)dt,\ f \in L_2(0,1),\ \varphi \in L_2(0,1),$$

$$H_\varphi : L_2(0,1) \to L_2(0,1)$$

have been investigated.

2. Some Evolutions of Numerical Radius for operator H_φ

To start with, prove the following result in special case of function φ.

Theorem 2.1. In case when

$$\varphi(x) = x^n,\ n = 0,1,2, \ldots.$$

$$\varphi : [0,1] \to \mathbb{R}$$

is true

$$\|H_\varphi\| \le \sqrt{\frac{1}{(2n+1)(2n+2)}}.$$

Proof. Indeed for any $f \in L_2(0,1)$ it is true

$$\|H_\varphi f\|^2 = \left\|\int_0^x t^n f(t)dt\right\|^2 = \int_0^1 \left|\int_0^x t^n f(t)dt\right|^2 dx$$

$$\le \int_0^1 \left|\int_0^x t^{2n} dt\ \left|\int_0^x |f|^2(t)dt\right| dx\right|$$

$$\le \int_0^1 \frac{x^{2n+1}}{2n+1} dx\ \|f\|^2 = \frac{1}{(2n+1)(2n+2)} \|f\|^2$$

Then it is obtained that

$$\|H_\varphi\| \leq \sqrt{\frac{1}{(2n+1)(2n+2)}}.$$

Now it will be given some results concerning to numerical radius of operator H_φ.

Theorem 2.2.

(1) If $\varphi(x) = x^n$, $n = 0,1,2, \ldots.$, then $w(H_\varphi) \leq \sqrt{\frac{1}{(2n+1)(2n+2)}}$;

(2) If $\varphi = P$ is polynomial function $P(x) = \sum_{k=0}^{m} a_k x^k$, $0 \leq x \leq 1$, then

$$w(H_\varphi) \leq \frac{a}{\sqrt{2}} \sum_{k=0}^{m} \sqrt{\frac{1}{(k+1)(2k+1)}} \ ;$$

(3) If $\varphi: [0,1] \to \mathbb{R}$ is a continuous function, then

$$w\left(H_\varphi\right) = \lim_{n\to\infty} w(P_n),$$

where $P_n: [0,1] \to \mathbb{R}$ is a polynomial function sequences, such that (P_n) uniformly converges to the function φ in $[0,1]$.

Proof.

(1) For any $f \in L_2(0,1)$, $\|f\| = 1$ we have

$$\left|(H_\varphi f, f)\right| = \left|\int_0^1 \int_0^x t^n f(t) dt\, \overline{f(x)} dx\right|$$

$$\leq \int_0^1 \left(\int_0^x t^n [f(t)] dt\right) |f(t)| dx$$

$$\leq \left(\int_0^1\left|\int_0^x t^n|f|(t)dt\right|^2 dx\right)^{1/2}\left(\int_0^1|f|^2(x)dx\right)^{1/2}$$

$$\leq \left(\int_0^1\left[\left(\int_0^x t^{2n}dt\right)^{1/2}\left(\int_0^x|f|^2(t)dt\right)^{1/2}\right]^2 dx\right)^{1/2}\|f\|$$

$$\leq \left(\int_0^1\left(\int_0^x t^{2n}dt\right)dx\right)^{1/2}\|f\|^2$$

$$= \left(\int_0^1 \frac{x}{2n+1}dx\right)^{1/2}\|f\|^2$$

$$= \sqrt{\frac{1}{(2n+1)(2n+2)}}\|f\|^2$$

Then for $\varphi(x) = x^n$, $n = 0,1,2,\ldots$. Is true

$$w(H_\varphi) \leq \sqrt{\frac{1}{(2n+1)(2n+2)}}\ ;$$

(2) Now let us $\varphi(x) = P(x) = \sum_{k=0}^{m} a_k x^k$, $a_k \in \mathbb{C}$, $k = 0,1,2,\ldots,m$. Then by subadditivity and absolute homogeneity properties of numerical radius function it is established that

$$w(H_P) \leq \sum_{k=0}^{m}|a_k|w\left(\int_0^x t^k f(t)dt\right)$$

$$\leq \sum_{k=0}^{m}|a_k|\sqrt{\frac{1}{(2k+1)(2k+2)}}$$

$$\leq \frac{a}{\sqrt{2}}\sum_{k=0}^{m}\sqrt{\frac{1}{(k+1)(2k+1)}},$$

where $a = \max_{0\leq k\leq m}|a_k|$.

Then

$$w(H_\varphi) \le \frac{a}{\sqrt{2}} \sum_{k=0}^{m} \sqrt{\frac{1}{(k+1)(2k+1)}}\ ;$$

(3) If $\varphi \in C[0,1]$, then by Weierstrass's Theorem there exists the polynomial function sequences (P_n) in [0,1], such that (P_n) uniformly converges to function φ with supremum metric. Then

$$\|(H_\varphi - H_{P_n})f\|^2 = \int_0^1 |H_n f - H_{P_n} f|^2 dx$$

$$= \int_0^1 \left|\int_0^x \varphi(t)f(t)dt - \int_0^x P_n(t)f(t)\right|^2 dx$$

$$\le \int_0^1 \left(\int_0^x |\varphi(t) - P_n(t)| f(t)dt\right)^2 dx$$

$$\le (\sup_{0\le t\le 1}|\varphi - P_n|(t))^2 \int_0^1 \left(\int_0^x |f(t)|dt\right)^2 dx$$

$$\le \|\varphi - P_n\|_C \int_0^1 x\left(\int_0^x |f|^2(t)dt\right)dx$$

$$\le \frac{1}{2}\|\varphi - P_n\|_C^2 \|f\|^2, \qquad f \in L^2(0,1),$$

$n \ge 1$.

Because

$$\|H_\varphi - H_{P_n}\| \le \frac{1}{\sqrt{2}}\|\varphi - P_n\|_C, n \ge 1.$$

Hence the operator sequences (H_{P_n}) converges to the operator H_φ in operator norm. Consequently, by Theorem (see [12]), it is obtained that

$$w(H_\varphi) = \lim_{n\to\infty} w(P_n).$$

Note that the last equality is not depended of polynomial sequences (P_n) which uniformly converges to the function φ.

Indeed, if there is another operator sequences (θ_n) converging to the function φ, then

$$\|P_n - \theta_n\|_C \leq \|P_n - \varphi\|_C + \|\varphi - \theta_n\|_C \xrightarrow[n\to\infty]{} 0 \, .$$

In this case, the numerical radius function's subadditivity property implies that

$$|w(P_n) - w(\theta_n)| \leq w(P_n - \theta_n) \leq \|P_n - \theta_n\|_{L^2}$$

$$\leq \|P_n - \theta_n\|_C \leq \|P_n - \varphi\|_C +$$

$$\|\varphi - \theta_n\|_C \xrightarrow[n\to\infty]{} 0 \, .$$

Then in part (3) of this theorem the polynomial function sequences (P_n) can be choosing in any way.

Example. Let us

$$\varphi(x) = e^x, 0 \leq x \leq 1, \varphi\colon [0,1] \to \mathbb{R} \, .$$

Then it is well known that the following polynomial sequences

$$P_n(x) = \sum_{k=0}^{n} \frac{x^k}{k!}, 0 \leq x \leq 1, k = 0,1,2, \ldots.$$

uniformly converges to φ in supremum norm.

Hence by Theorem 2.2 (2) we have

$$w(H_{P_n}) \leq \frac{1}{\sqrt{2}} \sum_{k=0}^{n} \sqrt{\frac{1}{(k+1)(2k+1)}} \frac{1}{k!}$$

$$\leq \frac{1}{\sqrt{2}}\sum_{k=0}^{n}\frac{1}{k!} \leq \frac{1}{\sqrt{2}}e, \quad n \geq 1.$$

Then by Theorem 2.2 (3) it implies that

$$w\left(H_\varphi\right) = \lim_{n\to\infty} w\left(H_{P_n}\right) \leq \tfrac{1}{\sqrt{2}}e\ .$$

Theorem 2.3. If $\varphi \in L_2(0,1)$ are true:

(1) $\left\|H_\varphi\right\| \leq \|\varphi\|$;

(2) $w\left(H_\varphi\right) \leq \left(\int_0^1\left(\int_0^x|\varphi|^2(t)\,dt\right)dx\right)^{1/2}$.

Proof.

(1) In this case for any $f \in L_2(0,1)$ we have

$$\begin{aligned}\left\|H_\varphi f\right\|^2 &= \int_0^1\left|\int_0^x \varphi(t)f(t)dt\right|^2dx\\ &\leq \int_0^1\left(\int_0^x|\varphi|^2(t)dt\right)\left(\int_0^x|f|^2(t)dt\right)dx\\ &\leq \int_0^1|\varphi|^2(t)dt\ \int_0^1|f|^2(t)dt\\ &= \|\varphi\|_{L^2}^2\ \|f\|^2.\end{aligned}$$

Then $\left\|H_\varphi\right\| \leq \|\varphi\|$.

(2) For any $f \in L_2(0,1)$, $\|f\| = 1$ it is obtained that

$$\left|\left(H_\varphi f, f\right)\right| \leq \int_0^1\left|\int_0^x \varphi(t)f(t)dt\right|\overline{f(x)}dx$$

$$\leq \left(\int_0^1\left|\int_0^x \varphi(t)f(t)dt\right|^2dx\right)^{1/2}\left(\int_0^1|f|^2(x)dx\right)^{1/2}$$

$$\leq \left(\int_0^1\left(\int_0^x|\varphi|^2(t)dt\right)\left(\int_0^x|f|^2(t)dt\right)dx\right)^{1/2}$$

$$= \left(\int_0^1\left(\int_0^x|\varphi|^2(t)dt\right)dx\right)^{1/2}.$$

Remark. Keep in mind that the operator H_φ can be expressed as

$$H_\varphi = VM_\varphi \, ,$$

where M_φ, $M_\varphi f(x) = \varphi(x)f(x)$, $f \in L_2(0,1)$ is a multiplication operator in $L_2(0,1)$ and V, $Vf(x) = \int_0^x f(t)dt$, $f \in L_2(0,1)$ is the classical Volterra integration operator in $L_2(0,1)$. Then on the numerical radius of product of two operators we have

$$w\left(H_\varphi\right) \leq 4w(V)w\left(M_\varphi\right) \leq 2w(M_\varphi) \, .$$

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Chapter 3

COUMARIN BASED POLYMERS: DESIGN STRATEGIES, FUNCTIONALIZATION, AND EMERGING APPLICATIONS

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Heterocyclic polymers are a unique class of polymers characterized by the inclusion of heterocyclic rings in their backbone structure. These polymers are widely studied due to their distinctive chemical and physical properties, which arise from the incorporation of heteroatoms (atoms other than carbon, typically nitrogen, oxygen, or sulfur) into the ring structure. The presence of heteroatoms in the ring not only alters the electronic properties of the polymer but also affects its thermal stability, mechanical strength, and solubility, making them highly attractive for a variety of applications, from electronic devices to biomedical materials (Alsolami et al., 2024).

In heterocyclic polymers, the heterocyclic rings are usually formed through the polymerization of monomers containing one or more heteroatoms. Some heterocyclic compounds commonly used are shown in Figure 1. The incorporation of these heteroatoms leads to a variety of structural motifs and functionalities, such as pyrrole, thiophene, imidazole, and pyridine-based structures, each with specific characteristics that influence the properties of the resulting polymer. These structural features allow for the creation of materials with tailored properties for particular uses (Murugan, 2023).

One of the most important types of heterocyclic polymers are those based on aromatic heterocycles. These materials often exhibit high chemical stability and resistance to oxidation, making them suitable for use in harsh environments. For example, poly(phenylene sulfide) (PPS) is a heterocyclic polymer that is known for its excellent chemical resistance, high thermal stability, and good electrical insulating properties. PPS is widely used in automotive and industrial applications, particularly in environments requiring resistance to high temperatures and aggressive chemicals (Cao et al., 2021).

Another prominent category of heterocyclic polymers is those derived from pyrrole and its derivatives. Polypyrrole, a conducting polymer, is one of the most studied materials in this class due to its ability to conduct electricity when doped with an appropriate oxidizing agent. Polypyrrole has shown promise in various applications owing to its flexible, lightweight nature and tunable conductivity. The ease of polymerization and doping of polypyrrole makes it a versatile material for electronic applications, especially in the field of organic electronics (Hao et al., 2024).

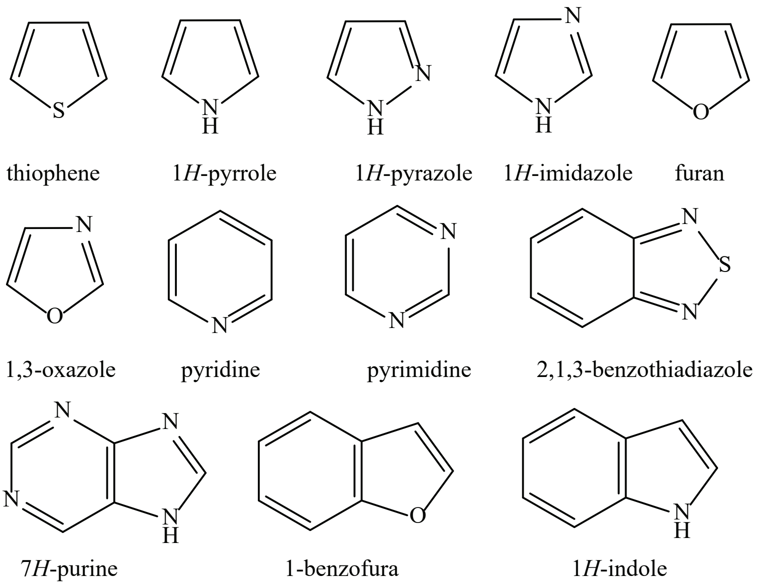

Figure 1. Some heterocyclic compounds commonly used.

In addition to their electrical properties, heterocyclic polymers can exhibit unique optical, mechanical, and thermal properties depending on the structure of the heterocyclic rings incorporated into the polymer backbone. For instance, polymers based on benzothiadiazole and other related heterocycles have been found to exhibit strong photoconductive properties, making them useful in solar cells and other photonic devices. These materials can also be engineered to have high thermal stability, which is essential for their use in aerospace and electronics applications where materials must withstand extreme temperatures (Cong et al., 2023).

The synthesis of heterocyclic polymers can be achieved through several different polymerization techniques, including condensation, addition, and ring-opening polymerization, etc. The choice of polymerization method depends on the specific heterocyclic monomer being used and the desired properties of the final polymer. For example, polyimides, which are polymers containing imide groups, are typically synthesized via a condensation reaction between diamines and dianhydrides (Yu et al., 2024).

A significant advantage of heterocyclic polymers is their versatility in modifying the polymer structure to obtain materials with highly specific properties. By altering the nature and arrangement of the heteroatoms in the heterocyclic rings, it is possible to tailor the material properties for specific applications. For example, introducing oxygen atoms into the polymer backbone can improve the solubility of the polymer, making it easier to process (Namsheer & Rout, 2021). On the other hand, introducing nitrogen or sulfur atoms can enhance the conductivity or provide specific interactions with other molecules, such as in the case of sensor materials or drug delivery systems.

The incorporation of heterocyclic units into the polymer backbone also has implications for the polymer's biodegradability and biocompatibility. In the field of biomaterials, heterocyclic polymers are being investigated for use in controlled drug release, tissue engineering, and other medical applications. Polymers such as poly(ethylene imine) and poly(lysine) contain nitrogen-based heterocycles, and they have shown promise in gene therapy and drug delivery due to their ability to interact with nucleic acids and other biological molecules (Pack et al., 2005). These polymers can also be engineered to be biodegradable, which is crucial for applications where the material must be broken down in the body over time.

One challenge in the development of heterocyclic polymers is the synthesis of high molecular weight materials. Many heterocyclic monomers tend to undergo side reactions or decomposition at high temperatures, which can limit the molecular weight of the resulting polymer. To address this, researchers have developed advanced polymerization techniques, such as catalytic polymerization like Cu-catalyzed, catalyst-free, multicomponent polymerizations, multicomponent tandem polymerizations, Passerini reactions, sequence- and controlled-multicomponent polymerization, and microwave-assisted synthesis, which allow for the control of polymer molecular weight and the avoidance of undesirable side reactions (Alsolami et al., 2024). These advancements are helping to improve the scalability and efficiency of heterocyclic polymer synthesis.

As explained above, heterocyclic polymers are a diverse and versatile class of materials with a broad range of potential applications across various industries. Their unique chemical structure, featuring heteroatoms in the polymer backbone, imparts a combination of desirable properties such as improved thermal stability, chemical resistance, conductivity, and biodegradability. The ongoing development of new synthesis techniques and the exploration of novel monomers continue to drive advancements in this field.

Among the many subclasses of heterocyclic compounds, oxygen-containing heterocycles hold particular significance due to their prevalence in natural products and bioactive molecules. One notable group within this category is coumarins (2H-chromen-2-one, also known as 2H-1-benzopyran-one), a class of benzopyrone derivatives characterized by a fused benzene and α-pyrone ring system. Figure 2 shows a schematic representation of the coumarin molecule. Coumarins are naturally occurring compounds derived from plants. Due to their diverse pharmacological, biochemical, and electro-optic properties, they have broad applications in various scientific and technological fields, particularly in medicine and pharmacy. Their pharmacological effects include anti-inflammatory, anticoagulant, antibacterial, antifungal, anticancer, antihypertensive, antitubercular, antioxidant, and protective properties (Venugopala et al., 2023; Soine, 1964; Sharma & Pritmani, 1999; Patonay et al., 1984; Shaker, 1996; Emmanuel-Giota et al., 2001; Nofal et al., 2000; Özkaya & Türkan, 2021). These compounds are commonly found in a wide range of dietary sources such as vegetables, fruits, seeds, nuts, coffee, and tea. Their low toxicity, affordability, presence in herbal medicines, and inclusion in dietary regimens suggest that their potential applications will continue to expand in the future (Venugopala et al., 2023).

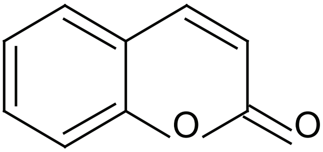

Figure 2. A schematic representation of the coumarin molecule.

As noted, coumarins belong to the phenolic compound class and have numerous derivatives. While some early pharmacological studies have been reviewed, more complex investigations have examined the chemical structures and biochemical properties of both simple and intricate natural coumarins (Lake, 1999). Coumarin molecules occur naturally, and many of their derivatives can also be synthesized in the laboratory using several well-known methods, including Pechmann condensation, von Pechmann condensation, Perkin reaction, Knoevenagel condensation, and Michael addition, etc. (Adimule et al., 2022). Their physicochemical, biochemical, pharmacological, electro-optical, and liquid crystal properties—as well as their therapeutic and technological applications—depend on the substituents attached to the coumarin backbone and their corresponding chemical characteristics.

Coumarin compounds, in the form of small organic molecules, play a significant role in polymer chemistry and technology beyond the application areas mentioned above. Their cyclic structure, π-conjugated system, and hyperconjugation, along with the ability to bind various substituted groups with donor or acceptor properties, contribute to the unique characteristics of coumarin-derived polymers. The coumarin structure can be present either in the main chain or the side group of these polymers, and the polymer itself can have a linear or network structure. These polymers have gained attention for their thermal, mechanical, morphological, rheological, dielectric, and electro-optic properties. Consequently, they have been the focus of extensive research in recent years and have been incorporated into numerous technological applications.

Coumarin-derived polymers are synthesized using various methods, including free radical polymerization, step-growth polymerization, and controlled/living polymerization techniques. One common approach involves incorporating coumarin-functionalized monomers into polymer backbones through radical polymerization, enabling tunable thermal, optical and mechanical properties. Patel and colleagues (2008) reported one such approach, where they synthesized and analyzed a new acrylic monomer, 7-acryloyloxy-4-methyl coumarin, along with its copolymers with methyl acrylate (Figure 3). Their study employed free radical polymerization at 70°C using an AIBN initiator. Characterization results indicated that as the mole fraction of coumarin monomer increased in the copolymer chain, the molecular weight also rose. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) suggested moderate thermal stability. The antimicrobial activities of copolymers varied depending on the coumarin content within the polymer structure.

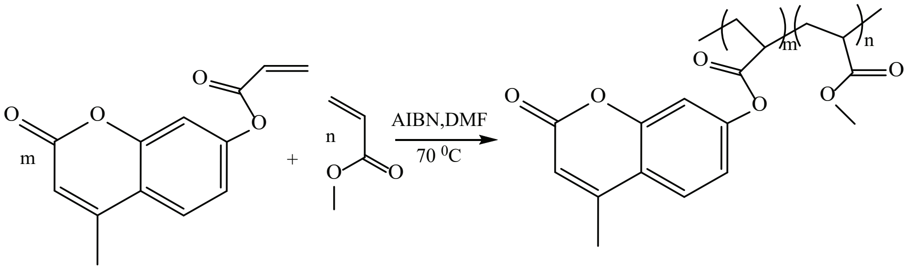

Figure 3. Copolymerization of 7-acryloyloxy-4-methyl coumarin and methyl acrylate.

Another significant method for synthesizing coumarin polymers is polycondensation method. Fomine et al. (1998) demonstrated this approach by synthesizing novel coumarin-based monomers and polymerizing them through high-temperature polycondensation, resulting in hyperbranched and comb-shaped coumarin polymers The synthesis scheme of one of these polymers is given in Figure 4. These polymers, exhibiting amorphous structures, were soluble in chlorinated aliphatic hydrocarbons and had molecular weights ranging from 2.000 to 50.000. Films produced by solution casting demonstrated high optical quality, with glass transition temperatures between 100°C and 230°C and thermal stability between 370°C and 415°C. The polymers were active in the blue light-emitting spectrum (450-492 nm).

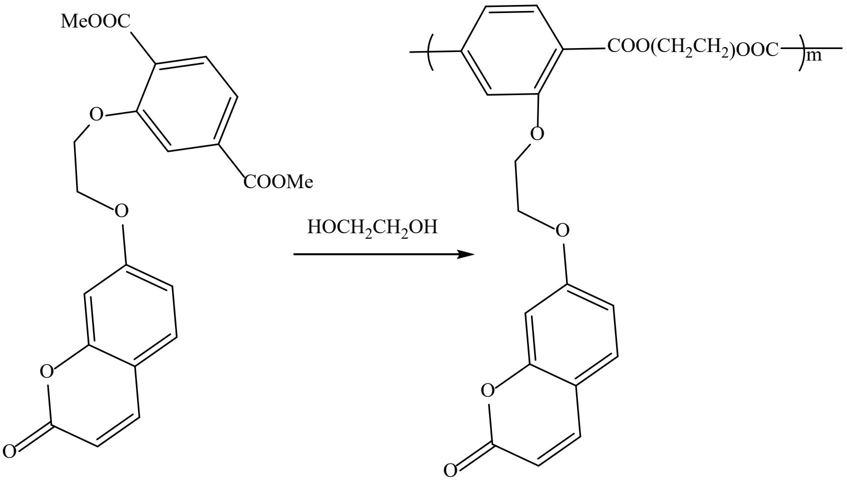

Figure 4. A Coumarin derived polymer obtained through the polycondensation method.

Coumarin-based polymers exhibit unique thermal properties due to their conjugated structure and photo-responsive characteristics. They generally have high thermal stability, with decomposition temperatures often exceeding ≈300°C, depending on their molecular weight and cross-linking density. Their glass transition temperatures vary widely, typically ranging from ≈100°C to ≈200°C, influenced by side-chain modifications and polymer backbone rigidity. In addition, coumarin polymers can undergo reversible photodimerization and cleavage upon UV irradiation, affecting their thermal behavior. Their thermal conductivity is relatively low, making them suitable for insulating applications similar to other commercial polymers. Depending on the synthesis method, coumarin polymers may exhibit thermoplastic or thermosetting behavior.

Thermal stability is a key consideration for coumarin-based polymers as mentioned above. Studies employing thermogravimetric analysis have been conducted to investigate the thermal decomposition kinetics of these polymers. For instance, a study on a copolymer system based on 3-benzoyl coumarin monomer and methyl methacrylate provides insight into the thermal stability and degradation behavior of the copolymer as shown in Figure 5. The results indicate that the temperature at which the maximum rate of weight loss occurs increases with the heating rate. Specifically, at a heating rate of 5 °C/min, the temperature is 384.81 °C, whereas at 20 °C/min, it rises to 407.45 °C. The activation energy, which represents the energy required to initiate decomposition, is determined using two different methods, Kissinger's and Flynn–Wall–Ozawa methods. The activation energy can be calculated directly using these two methods, which are independent of the reaction order. Kissinger's method yields a value of 212.98 kJ/mol, while the Flynn–Wall–Ozawa method gives 210.30 kJ/mol. These values are calculated within the conversion range of 9%–21%. The increase in temperature with heating rate suggests a dependency on the heat transfer process, while the activation energy values indicate the energy required for decomposition. To further analyze the thermal decomposition process, several kinetic models, including Coats-Redfern, Tang, Madhusudanan, and Van-Krevelen, are employed. The results show that the copolymer decomposition follows a D_3 mechanism, which corresponds to a three-dimensional diffusion-controlled solid-state reaction. This indicates that thermal decomposition is primarily governed by the diffusion of volatile products through the solid matrix, which is crucial for applications where thermal stability is a critical factor (Kurt et al., 2019).

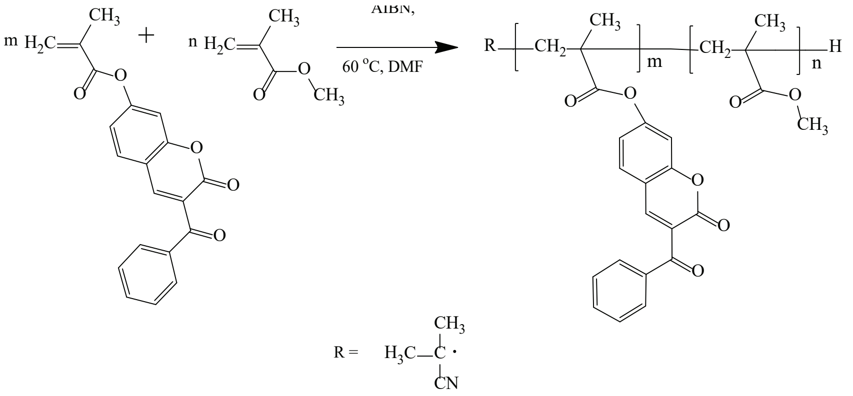

Figure 5. Polymerization of 3-benzoyl coumarin derived monomer and methyl methacrylate via free radical mechanism.

Similarly, a study was conducted on a homopolymer containing a coumarin side group, specifically poly(3-benzoyl coumarin-7-yl-methacrylate). The research utilized thermogravimetric analysis to investigate the polymer's thermal behavior at different heating rates. The findings indicated that the polymer's thermal stability increases with higher heating rates. The activation energy of decomposition was determined using two kinetic methods: the Flynn-Wall-Ozawa method (155.01 kJ/mol) and the Kissinger method (165.29 kJ/mol). The kinetic calculation equations used in these two methods are commonly found in the literature. For example, Figure 6 presents the Ozawa and Kissinger lines, which are drawn based on the evaluation of data obtained from experiments to analyze the thermal decomposition kinetics of this polymer. Similar to many other polymers, the Ozawa curves for the current coumarin polymer are almost entirely parallel within the specified decomposition ranges. This parallelism remains valid as long as there are no significant deviations in the experimental data. Furthermore, the presence of this parallelism enhances the reliability of the results and, consequently, the correlation. The decomposition mechanism was analyzed using the Coats-Redfern method, revealing that the thermal decomposition follows a D_1 one-dimensional diffusion-type deceleration mechanism at an optimal heating rate of 10 °C/min. This study also provides valuable insights into the thermal stability and degradation behavior of this novel coumarin-based methacrylate polymer, contributing to a better understanding of its potential suitability for high-temperature applications in various fields (Kurt, 2017).

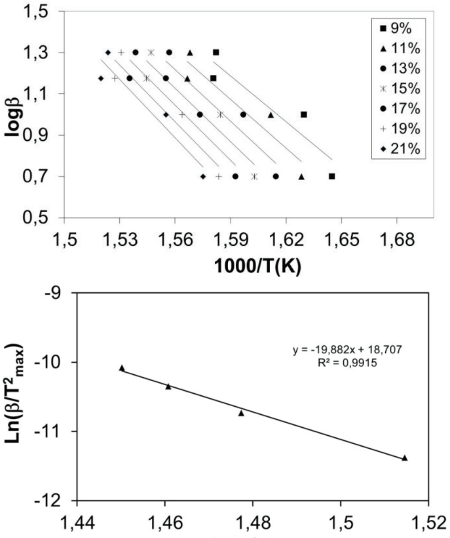

Figure 6. Kinetic figures using the Flynn-Wall-Ozawa and Kissinger methods, respectively

Venkatesan et al. conducted a study on coumarin-based methacrylate copolymers, focusing on their synthesis, thermal stability, and antibacterial activity. They synthesized and characterized 7-methacryloyloxy-4-methyl coumarin monomer and polymerized it with butoxy ethyl methacrylate. Their findings indicated moderate thermal stability, with higher glass transition temperatures and antibacterial activity increasing as the coumarin content increased. In addition to these findings, their study was published to contribute to the existing research in this field (Venkatesana et al., 2014).

Coumarin polymers exhibit unique photophysical properties due to the presence of conjugated π-electron systems and their ability to undergo photodimerization and photocleavage under UV light. These polymers typically display strong fluorescence in the ultraviolet to visible range, with emission characteristics influenced by factors such as molecular structure, solvent polarity, and polymer backbone rigidity. The fluorescence quantum yield and lifetime of these polymers can be tuned by modifying substituents or incorporating functional groups that affect electronic transitions. The photochemical behavior of coumarin derivatives is influenced by their molecular structure; for example, expanding the π-electron system along the carbon-3 and 4 bond of the coumarin skeleton enhances fluorescence quantum yields. Additionally, introducing substituents like alkoxy groups at the 7-position can modulate the aggregation behavior and electrical properties of thin films made from these polymers. Moreover, the incorporation of coumarin moieties into polymer chains can influence the thermal and structural properties of the resulting materials. A research indicates that the composition of the side group plays a crucial role in determining the liquid crystalline properties of polymers. For instance, Tian et al. (2000) synthesized polymethacrylate polymers containing 7-benzoyloxy coumarin side groups, investigating the effects of substitution positions on their liquid crystal behavior. Polymers substituted at the 3-position of the coumarin ring exhibited a mesophase over a broad temperature range, while those at the 4-position did not form a mesophase. Additionally, the polymers tended to exhibit either a glassy or crystalline state, depending on the specific side group structure.

Coumarin polymers also exhibit significant nonlinear optical (NLO) properties due to their unique molecular structure, which includes conjugated systems that enhance electron delocalization. These polymers are known for their high third-order NLO responses, making them suitable for electro-optic applications. These compounds are well-known for their photochemical and photophysical properties. Upon irradiation (>300 nm), they reversibly form cyclobutane-based dimers as schematized in

Figure 7. The presence of functional groups in coumarin derivatives allows for tunable optical characteristics, such as absorption and emission wavelengths. Additionally, the nonlinear refractive index and second-order susceptibility of these polymers make them ideal candidates for advanced photonic devices.

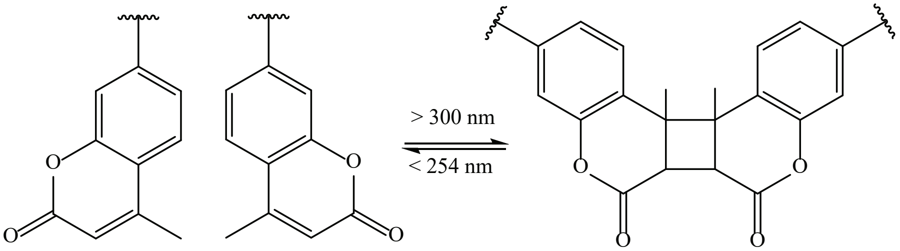

Figure 7. A reversible photoinduced cyclodimerisation of coumarins for NLO properties.

Essaidi and colleagues (2013) investigated photo-crosslinkable coumarin-based copolymers and their second-order nonlinear optical properties. Their research involved high-quality, transparent thin films of methacrylic copolymers containing a 4-methyl coumarin chromophore. Nonlinear optical properties were studied using Nd:YAG laser irradiation at 1064 nm. Exposure to light at 254 nm and 300 nm induced reversible photo-dimerization of coumarin molecules, significantly influencing their nonlinear optical behavior.

Another study by Skowronski and his team (2015) examined the optical properties of coumarin-containing copolymers, analyzing absorption coefficients, refractive indices, dielectric function parameters, and energy band gaps through spectroscopic ellipsometry, atomic force microscopy, and transmittance measurements. Their findings showed that the optical properties of these copolymers were significantly influenced by the alkyl chain length and the substitution patterns within the coumarin structure. An increase in alkyl chain length resulted in bathochromic shifts in the absorption spectra.

In addition, methacrylic coumarin polymers have garnered significant attention in the field of non-linear optical data storage due to their unique photochemical properties. These polymers incorporate coumarin derivatives, which are known for their ability to undergo photodimerization—a process where two coumarin molecules react under light exposure to form a dimer. This reversible reaction allows for the writing and erasing of data within the polymer matrix. A comprehensive study published in the journal *Molecules* by Gindre et al. (2016) explored the synthesis, characterization, and non-linear optical properties of a series of methacrylic copolymers containing coumarin side groups. The research demonstrated that these copolymers could undergo reversible photodimerization upon exposure to femtosecond laser pulses, enabling high-density optical data storage. The study also highlighted the use of second harmonic generation microscopy as a readout method, allowing for precise detection of stored information. In addition to photodimerization, the two-photon absorption properties of coumarin derivatives have been utilized for optical data storage. By employing appropriate irradiation wavelengths, recording and erasing processes can be conducted within the same area of the polymer film. This method takes advantage of the coumarin-containing polymers' non-linear optical properties to enable high-density data storage.

Coumarin-based polymer-clay nanocomposites have garnered considerable interest due to their enhanced mechanical, thermal, and optical properties, which arise from the synergistic effects of coumarin functionalities and clay nanofillers. These materials are synthesized by incorporating coumarin-modified polymers with clay minerals, leading to nanocomposites with improved performance characteristics. Clay, a commonly used nanofiller, is favored for its affordability, ease of availability, and superior properties. Before its incorporation into polymeric materials, clay undergoes an organic modification process. The organo-modified clay is then introduced into the polymer matrix using appropriate methods outlined in the literature. In recent years, coumarin-based polymers have been extensively utilized for the preparation of polymeric nanocomposites with various reinforcing elements, with clay being one of the most widely used.

Our research group conducted a study in this field, reporting the synthesis of poly(3-benzoyl coumarin-7-yl-methacrylate) and its nanocomposites with montmorillonite clay. Characterization techniques such as fourier-transform infrared spectroscopy, X-ray diffraction analysis (XRD), differential scanning calorimetry, and thermogravimetric analysis were employed. XRD analysis indicated a shift from exfoliated to intercalated morphologies as the clay content increased from 1% to 5%. DSC analysis showed a partial increase in glass transition temperatures with higher clay ratios, while TGA analysis demonstrated enhanced thermal stability with increasing clay content (Kurt & Topsoy, 2017).

Significant delays in thermal degradation were observed depending on the contribution rate of clay reinforcement. One of the main reasons for this is that the polymer molecules respond to the applied thermal effect with a delay due to the homogeneous and nano-sized distribution of clay layers between the polymer chains. As a result, these clay layers act as a barrier between the heat source and the polymer chains, enhancing thermal stability. For instance, Figure 8 presents a typical TGA thermogram of coumarin-derived polymer/clay nanocomposites. Similar thermal behaviors are also observed in other polymeric nanocomposite systems containing clay.

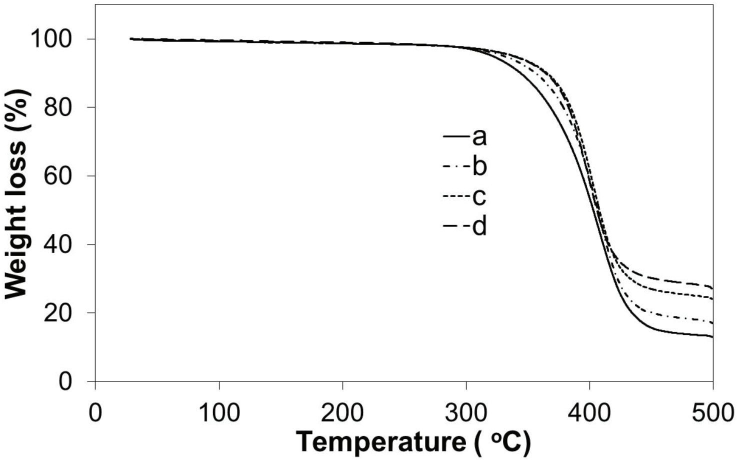

Figure 8. TGA curves: a) homopolymer and b) 1%, c) 3%, d) 5% clay doped nanocomposites

In another study, Kurt and Koca (2016) synthesized a novel polymer derived from coumarin, poly(3-acetyl coumarin-7-yl-methacrylate), and developed nanocomposites reinforced with organomodified clay. Spectral characterization confirmed the successful synthesis of the polymer and nanocomposites. Thermal stability assessments indicated that the incorporation of organoclay enhanced the thermal stability of the nanocomposites, with the 4 wt% organoclay nanocomposite showing the best thermal stability at 319°C. XRD analysis revealed exfoliated clay dispersion within the polymer matrix as shown in Figure 9.

Since all peaks originating from organoclay in polymer clay mixtures have completely disappeared, this shows that the clay layers are fully dispersed in the polymer, meaning exfoliated type nanocomposites have been formed. This situation is important in terms of providing insight into how nanocomposites behave with the addition of clay. Polymer-clay nanocomposites that exhibit an exfoliated-type behavior are not sensitive to XRD. When the clay layers are fully dispersed (i.e., exfoliated), no layered structure remains to alter the direction of X-rays. As a result, according to Bragg's law, no peak will be observed, particularly in the 2-theta to 10-theta diffraction angle range. Similar patterns to the behavior of the XRD curves provided for the existing polymer in Figure 9 can be considered examples of exfoliated-type polymer-clay nanocomposites.

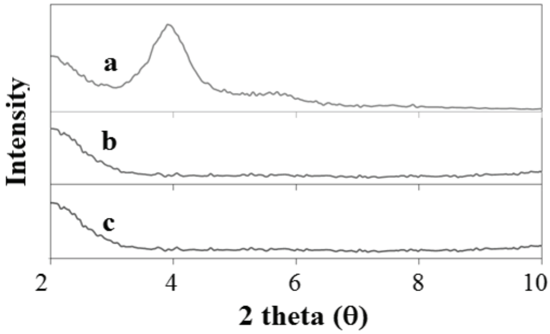

Figure 9. XRD patterns of a) organoclay, b) and c) exfoliated polymer/clay (2%,4%) nanocomposites

Kurt and coworkers (2016) explored the synthesis of a new coumarin-based surface-active monomer and its role in nanocomposite formation. The study involved the synthesis of 4-chloromethyl coumarin-7-yl-methacrylate monomer (numbered as 2), followed by its alkylation with N,N-dimethyl hexadecyl amine to produce a surfactant compound. The scheme of this experimental procedure was given in Figure 10. This surfactant (3) was used to modify natural montmorillonite clay, creating a coumarin-derived organomodified clay. Figure 11 proposed a scheme for the coumarin-derived organomodified clay. Poly(methyl methacrylate)-organo clay nanocomposites were prepared with varying organoclay content (1-5%). XRD analysis confirmed exfoliated clay structures, while the TGA results showed that an increase in clay loading corresponded to enhanced thermal stability.

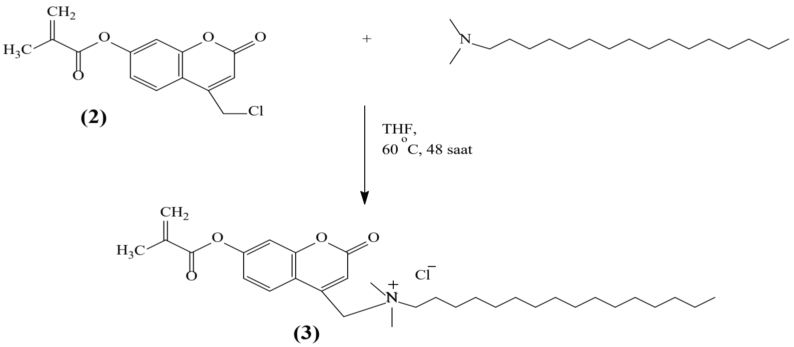

Figure 10. Coumarin-based surface-active monomer.

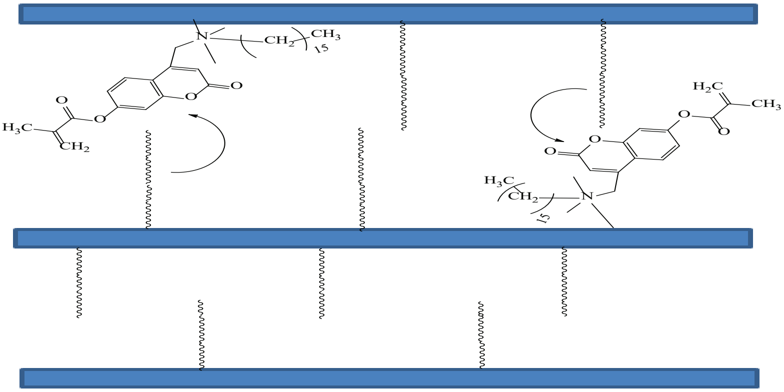

Figure 11. A scheme proposed for a coumarin-derived organomodified clay.

Additionally, coumarin-based polymers exhibit intriguing thermo-responsive properties, making them valuable in various technological applications. These polymers undergo reversible structural or phase changes in response to temperature variations, often due to the presence of coumarin moieties that enable light-induced dimerization and thermal cleavage. The lower critical solution temperature (LCST) behavior of coumarin polymers can be finely tuned by modifying their chemical composition, molecular weight, or incorporating hydrophilic and hydrophobic segments. Upon heating, coumarin-containing polymers can undergo chain scission or crosslinking, influencing their solubility, viscosity, or mechanical strength. This distinctive thermal responsiveness enables the use of coumarin polymers in controlled drug delivery systems, where temperature activates the release of encapsulated drugs, as well as in photo-reversible materials that display adjustable properties when exposed to light and heat stimuli. The thermoresponsive properties of these polymers can be finely tuned through structural modifications. As reported in reference by Okada & Sato (2021), the phase transition temperature can be precisely controlled by introducing ethyleneoxy spacers or methyl groups to the coumarin units, which adjusts the LCST. Figure 12 shows these polymers.

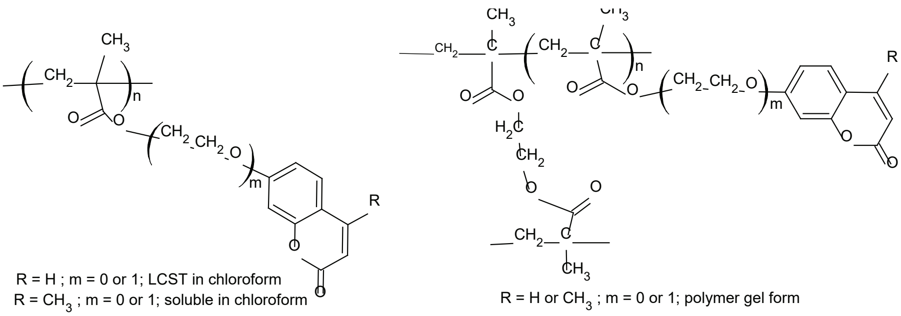

Figure 12. Coumarin polymer structures for thermo-responsive properties (Okada& Sato, 2021)

In conclusion, coumarin-based polymers are a versatile class of materials with broad applications in pharmaceuticals, advanced polymer science, optoelectronics, and nanocomposites. Their unique physicochemical, photophysical, and thermal properties, along with diverse synthesis methods, allow for tailored designs with enhanced stability and performance. Notably, their photoreactivity and nonlinear optical behavior make them valuable for modern photonic and data storage applications. Recent research highlights their role in improving thermal stability and mechanical properties, particularly in nanocomposites. As molecular engineering and functionalization techniques advance, coumarin-based polymers are expected to integrate with emerging technologies, solidifying their importance in next-generation material science and innovation.

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Chapter 4

QUANTUM CALCULUS APPROACH TO THE DUAL TESSARINE NUMBER SEQUENCES

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1. INTRODUCTION

Complex numbers were discovered by the Italian mathematician G. Cardano while he tries to solve a simpler state of the cubic equation and using the notation $i=\sqrt{-1}$. The complex numbers as points with rectangular coordinates were represented by Euler. After that, Cockle, (1849) proposed the tessarine numbers, an algebraic successor to complex numbers and quaternionic algebra, employing more modern notation. In the exponential series, he employed tessarine numbers to separate the hyperbolic sine and cosine series (Cockle, 1849; Cockle, 1850). Clifford defined the algebra of dual numbers as a fundamental tool for geometric investigations. Eduard Study utilized dual numbers and dual vectors in the study of line geometry and kinematics (Study, 2022), demonstrating a one-to-one correspondence between the points of the dual unit sphere (Guggenheimer, 2012; Fischer, 1998; Angeles, 1998).

Dual numbers as in the form $\mathbb{A}=a_0+\varepsilon a_1,$ where a_0 and a_1 are real numbers, and ε is an element with the property that $\varepsilon^2=0$, but $\varepsilon\neq 0$. The addition and multiplication of any dual numbers $\mathbb{A}$ and $\mathbb{B}$ are defined, respectively, as follows:

$\mathbb{A}+\mathbb{B}=(a_0+b_0)+\varepsilon(a_1+b_1)$

and

$\mathbb{A}\,\mathbb{B}=a_0\,b_0+\varepsilon(a_0\,b_1+a_1\,b_0).$

The set of tessarine numbers is defined by

$$\mathcal{T}=\{\gamma=\gamma_0+\gamma_1 i_1+\gamma_2 i_2+\gamma_3 i_3 : \gamma_0,\gamma_1,\gamma_2,\gamma_3 \epsilon \mathbb{R}\}$$

where i_1, i_2 and i_3 are the imaginary units which satisfy the following rules:

$$i_1^2=-i_2^2=i_3^2=-1\ ;\ i_1 i_2=i_2 i_1=i_3. \tag{1}$$

The addition and multiplication of tessarine numbers $\gamma=\gamma_0+\gamma_1 i_1+\gamma_2 i_2+\gamma_3 i_3$ and $\delta=\delta_0+\delta_1 i_1+\delta_2 i_2+\delta_3 i_3$ are defined, respectively, as:

$$\gamma+\delta=(\gamma_0+\delta_0)+(\gamma_1+\delta_1)i_1+(\gamma_2+\delta_2)i_2+(\gamma_3+\delta_3)i_3$$

and

$$\gamma\delta = \gamma_0\delta_0 - \gamma_1\delta_1 + \gamma_2\delta_2 - \gamma_3\delta_3 + (\gamma_0\delta_1 + \gamma_1\delta_0 - \gamma_2\delta_3 - \gamma_3\delta_2)i_1$$

$$+(\gamma_0\delta_2 + \gamma_2\delta_0 - \gamma_3\delta_1 - \gamma_1\delta_3)i_2 + (\gamma_0\delta_3 + \gamma_3\delta_0 + \gamma_1\delta_2 + \gamma_2\delta_1)i_3.$$

In mathematics, the Fibonacci numbers and Lucas numbers are an infinite sequences of integers in which each number is the sum of the two preceding ones. These numbers have been researched extensively because of their complex characteristics and deep connections to several fields of mathematics and their related numbers are of essential importance due to their various applications in biology, physics, statistics, and computer science (Horadam, 1961; Horadam, 1963; Nalli, & Haukkanen, 2009; Koshy, 2018; Koshy, 2019; Odual et al, 2020).

For n ≥ 2, the second order linear sequences F_n and L_n are defined by:

$$\begin{cases} F_n = F_{n-1} + F_{n-2} \\ L_n = L_{n-1} + L_{n-2.} \end{cases}$$

Here, the initial conditions are $F_0 = 0, F_1 = 1, L_0 = 2$ and $L_1 = 1$, respectively. The Binet formulas of these numbers are

$$\begin{cases} F_n = \dfrac{\alpha^n - \beta^n}{\alpha - \beta} \\ L_n = \alpha^n + \beta^n \end{cases}$$

where α and β are roots of characteristic equation $\varphi^2 - \varphi - 1 = 0$.
Now, we give definitions and facts from the quantum calculus necessary for understanding of this paper (Kac & Cheung, 2002,; Kome et. al. ,2022; Babadağ, 2023).
For any integers n and m, we define the function

$$[n]_q = \frac{1-q^n}{1-q} = 1 + q + \cdots + q^{n-1} \qquad (2)$$

and

$$\begin{cases} [m+n]_q = [m]_q + q^m[n]_q \\ \\ \ [mn]_q = [m]_q + [n]_{q^m} . \end{cases} \tag{3}$$

During the last few years, few researchers have studied the tessarine numbers with Fibonacci numbers, Lucas numbers , Homothetic Motions, Surfaces and Neural Networks (Babadağ, 2017; Babadağ, & Uslu, 2021; Senna & Valle, 2021). For example, Babadağ, & Uslu, (2021) defined the Fibonacci tessarines with Fibonacci and Lucas numbers, and they examined the identities related to the tessarines, Fibonacci numbers and Lucas numbers . Babadağ, (2017) defined the homothetic motions and homothetic exponential motions. Senna & Valle, (2021) give tessarine and quaternion-valued deep neural networks for image classification.
In this paper, using different perspective, we define the tessarine number sequences with components including quantum integers and get several new results for these number sequences. Section 2. we give the q-Fibonacci tessarine number sequences and q-Lucas tessarine number sequences. Section 3. we explore some identities used in various areas of mathematics, including Binet's formula, the exponential generating function, and Catalan, Cassini, and D'Ocagne's identities and we define quantum tessarine polynomial sequences or, briefly q-Fibonacci tessarine polynomial sequences $\gamma_{q,n}(t)$ and q-Lucas tessarine polynomial sequences $\delta_{q,n}(t)$ and then derive the Binet formula for these type of polynomial sequence. In addition some results of q-tessarine polynomial sequences are given. Then, we define quantum tessarine function sequences or briefly q-Fibonacci and q-Lucas tessarine function sequences $\Gamma_{q,n}(t)$ and $\Delta_{q,n}(t)$.

2. q-Fibonacci Dual Tessarine Numbers and q-Lucas Dual Tessarine Numbers

Quantum calculus are an important in physics, combinatorics, number theory and other fields of the mathematics. since quantum calculus may be viewed as generalization of ordinary calculus, there is a relationship between quantum calculus and number sequences

Definition 3.1. Dual tessarine number sequences of the form

$$\begin{aligned}\mathcal{T}f_n(\alpha,q) = {} & \alpha^{n-1}[n]_q + \alpha^n[n+1]_q i_1 + \alpha^{n+1}[n+2]_q i_2 \\ & + \alpha^{n+2}[n+3]_q i_3 \\ & +\varepsilon\big(\alpha^n[n+1]_q + \alpha^{n+1}[n+2]_q i_1 \\ & \quad + \alpha^{n+2}[n+3]_q i_2 + \alpha^{n+3}[n+4]_q i_3\big)\end{aligned} \tag{4}$$

are called the n^{th} q-Fibonacci dual tessarine number sequences and

$$\begin{aligned}\mathcal{T}l_n(\alpha,q) = {} & \alpha^n\frac{[2n]_q}{[n]_q} + \alpha^{n+1}\frac{[2n+2]_q}{[n+1]_q}i_1 + \alpha^{n+2}\frac{[2n+4]_q}{[n+2]_q}i_2 + \alpha^{n+3}\frac{[2n+6]_q}{[n+3]_q}i_3 \\ & +\varepsilon\left(\alpha^n\frac{[2n+2]_q}{[n]_q} + \alpha^{n+1}\frac{[2n+4]_q}{[n+1]_q}i_1 + \alpha^{n+2}\frac{[2n+6]_q}{[n+2]_q}i_2 + \alpha^{n+3}\frac{[2n+}{[n+3}\right.\end{aligned}$$

are called as the n^{th} q-Lucas dual tessarine number sequences. Furthermore, we can rewrite these number sequences in the following forms:

$$\begin{aligned}\mathcal{T}f_n(\alpha,q) = {} & \frac{\alpha^n(1-q^n)}{\alpha-\alpha q} + \frac{\alpha^{n+1}(1-q^{n+1})}{\alpha-\alpha q}i_1 + \frac{\alpha^{n+2}(1-q^{n+2})}{\alpha-\alpha q}i_2 \\ & + \frac{\alpha^{n+3}(1-q^{n+3})}{\alpha-\alpha q}i_3 \\ & + \\ & +\varepsilon\left(\frac{\alpha^n(1-q^n)}{\alpha-\alpha q} + \frac{\alpha^{n+1}(1-q^{n+1})}{\alpha-\alpha q}i_1 + \frac{\alpha^{n+2}(1-q^{n+2})}{\alpha-\alpha q}i_2\right. \\ & \left. \quad + \frac{\alpha^{n+3}(1-q^{n+3})}{\alpha-\alpha q}i_3\right)\end{aligned}$$

and

$$\begin{aligned}\mathcal{T}l_n(\alpha,q) = {} & \alpha^n\frac{1-q^{2n}}{1-q^n} + \alpha^{n+1}\frac{1-q^{2n+2}}{1-q^{n+1}}i_1 \\ & + \alpha^{n+2}\frac{1-q^{2n+4}}{1-q^{n+2}}i_2 + \alpha^{n+3}\frac{1-q^{2n+6}}{1-q^{n+3}}i_3 \\ & +\varepsilon\left(\alpha^n\frac{1-q^{2n}}{1-q^n} + \alpha^{n+1}\frac{1-q^{2n+2}}{1-q^{n+1}}i_1 + \alpha^{n+2}\frac{1-q^{2n+4}}{1-q^{n+2}}i_2\right. \\ & \left. \quad + \alpha^{n+3}\frac{1-q^{2n+6}}{1-q^{n+3}}i_3\right)\end{aligned} \tag{5}$$

where $i_1,\ i_2$ and i_3 are the imaginary units which satisfy the rules in (1).

Theorem 3.1. The Binet formulas for q-Fibonacci dual tessarine number sequences and q-Lucas dual tessarine number sequences are given by

$$\begin{cases} \mathcal{T}f_n(\alpha,q) = \left(\alpha^{n-1}[n]_q\underline{\alpha} + (\alpha q)^n\underline{\beta}\right) + \varepsilon\left(\alpha^n[n+1]_q\underline{\alpha} + (\alpha q)^{n+1}\underline{\beta}\right) \\ \mathcal{T}l_n(\alpha,q) = \alpha^n\dfrac{[2n]_q}{[n]_q}\underline{\gamma} + \alpha^{n+1}(1-q)\underline{\beta} + +\varepsilon\left(\alpha^n\dfrac{[2n+2]_q}{[n+1]_q}\underline{\gamma} + \alpha^{n+2}(1\right. \end{cases} \quad (6)$$

Moreover, these formulas can be rewritten in the form:

$$\begin{cases} \mathcal{T}f_n(\alpha,q) = \dfrac{\alpha^n\underline{\alpha} - (\alpha q)^n\underline{\varphi}}{\alpha - \alpha q} + \varepsilon\left(\dfrac{\alpha^{n+1}\underline{\alpha} - (\alpha q)^{n+1}\underline{\varphi}}{\alpha - \alpha q}\right) \\ \mathcal{T}l_n(\alpha,q) = \alpha^n\underline{\alpha} + (\alpha q)^n\underline{\varphi} + \varepsilon\left(\alpha^{n+1}\underline{\alpha} + (\alpha q)^{n+1}\underline{\varphi}\right) \end{cases} \quad (7)$$

where the terms $\underline{\alpha}$, $\underline{\beta}$, and $\underline{\varphi}$ are defined as follows:

$$\begin{cases} \underline{\alpha} = 1 + \alpha i_1 + \alpha^2 i_2 + \alpha^3 i_3 \\ \underline{\beta} = i_1 + \alpha[2]_q i_2 + \alpha^2[3]_q i_3 \\ \underline{\varphi} = 1 + (\alpha q)i_1 + (\alpha q)^2 i_2 + (\alpha q)^3 i_3. \end{cases} \quad (8)$$

Here, $[n]_q$ denotes the q-analog of n, and $i_1,\ i_2,\ i_3$ are the imaginary units satisfying the relations defined in (1) .

Proof. By using (2), (3), (4) and (8), we can write

$$\begin{aligned} \mathcal{T}f_n(\alpha,q) \quad &= \alpha^{n-1}[n]_q + \alpha^n[n+1]_q i_1 + \alpha^{n+1}[n+2]_q i_2 \\ &\quad + \alpha^{n+2}[n+3]_q i_3 \\ &\quad +\varepsilon\big(\alpha^n[n+1]_q + \alpha^{n+1}[n+2]_q i_1 + \alpha^{n+2}[n+3]_q i_2 \\ &\quad + \alpha^{n+3}[n+4]_q i_3\big) \\ &= \alpha^{n-1}[n]_q + \alpha^n\big([n]_q + q^n\big)i_1 + \alpha^{n+1}([n]_q + q^n[2]_q)i_2 \\ &\quad + \alpha^{n+2}([n]_q + q^n[3]_q)i_3 \end{aligned}$$

$$+\varepsilon\big(\alpha^{n}\big([n]_q+q^{n}\big)+\alpha^{n+1}([n]_q+q^{n}[2]_q)i_1+\alpha^{n+2}([n]_q+q^{n}[3]_q)i_2+\alpha^{n+3}([n]_q+q^{n}[4]_q)i_3\big)$$

$$=\Big(\alpha^{n-1}[n]_q(1+\alpha i_1+\alpha^2 i_2+\alpha^3 i_3)+\alpha^{n}q^{n}\big(i_1+\alpha[2]_q i_2+\alpha^2[3]_q i_3\big)\Big)$$

$$+\varepsilon\Big([n+1]_q(1+\alpha i_1+\alpha^2 i_2+\alpha^3 i_3)+\alpha^{n+1}q^{n+1}\big(i_1+\alpha[2]_q i_2+\alpha^2[3]_q i_3\big)\Big)$$

$$=\alpha^{n-1}[n]_q\underline{\alpha}+(\alpha q)^{n}\underline{\beta}+\varepsilon\Big(\alpha^{n}[n+1]_q\underline{\alpha}+(\alpha q)^{n+1}\underline{\beta}\Big).$$

For q-Lucas dual tessarine number sequences by using (2), (5) and (8):

$$\mathcal{T}l_n(\alpha,q)=\alpha^{n}\frac{1-q^{2n}}{1-q^{n}}+\alpha^{n+1}\frac{1-q^{2n+2}}{1-q^{n+1}}i_1+\alpha^{n+2}\frac{1-q^{2n+4}}{1-q^{n+2}}i_2+\alpha^{n+3}\frac{1-q^{2n+6}}{1-q^{n+3}}i_3$$

$$+\varepsilon\Bigg(=\alpha^{n+1}\frac{1-q^{2n+2}}{1-q^{n+1}}+\alpha^{n+2}\frac{1-q^{2n+4}}{1-q^{n+2}}i_1+\alpha^{n+3}\frac{1-q^{2n+6}}{1-q^{n+3}}i_2+\alpha^{n+4}\frac{1-q^{2n+8}}{1-q^{n+4}}i_3\Bigg)$$

$$=\alpha^{n}\underline{\alpha}+(\alpha q)^{n}\underline{\beta}+\varepsilon\Big(\alpha^{n+1}\underline{\alpha}+(\alpha q)^{n+1}\underline{\beta}\Big).$$

Theorem 3.2. (Exponential generating functions) The exponential generating functions for q-Fibonacci dual tessarine number sequences and q-Lucas dual tessarine number sequences are:

$$f(x)=\frac{e^{\alpha x}\underline{\alpha}-e^{(\alpha q)x}\underline{\underline{\varphi}}}{\alpha-\alpha q}+\varepsilon\left(\frac{e^{\alpha x}\alpha\underline{\alpha}-e^{(\alpha q)x}\alpha q\underline{\underline{\varphi}}}{\alpha-\alpha q}\right)$$

$$g(x)=e^{\alpha x}\underline{\alpha}+e^{(\alpha q)x}\underline{\varphi}+\varepsilon\Big(e^{\alpha x}\alpha\underline{\alpha}+e^{(\alpha q)x}\underline{\alpha q\underline{\varphi}}\Big)$$

respectively.

Proof. Using Binet-like formula for q-Fibonacci dual tessarine numbers and

$e^{\alpha x}=\sum_{n=0}^{\infty}\alpha^n\frac{x^n}{n!}$ we get:

$$f(x)=\sum_{n=0}^{\infty}\gamma_n\frac{x^n}{n!}=\frac{1}{\alpha-\alpha q}\sum_{n=0}^{\infty}\left(e^{\alpha x}\underline{\alpha}-e^{(\alpha q)x}\underline{\varphi}\right)\frac{x^n}{n!}$$
$$+\varepsilon\left(\frac{1}{\alpha-\alpha q}\sum_{n=0}^{\infty}\left(e^{\alpha x}\underline{\alpha}-e^{(\alpha q)x}\underline{\varphi}\right)\frac{x^n}{n!}\right)$$

$$=\frac{e^{\alpha x}\underline{\alpha}-e^{(\alpha q)x}\underline{\varphi}}{\alpha-\alpha q}+\varepsilon\left(\frac{1}{\alpha-\alpha q}\sum_{n=0}^{\infty}\left(e^{\alpha x}\alpha\underline{\alpha}-e^{(\alpha q)x}\alpha q\underline{\varphi}\right)\frac{x^n}{n!}\right)$$

Moreover, from (7), we get

$$g(x)=\sum_{n=0}^{\infty}\gamma_n\frac{x^n}{n!}=\sum_{n=0}^{\infty}\left(e^{\alpha x}\underline{\alpha}+e^{(\alpha q)x}\underline{\varphi}\right)\frac{x^n}{n!}+\varepsilon\left(\sum_{n=0}^{\infty}\left(e^{\alpha x}\alpha\underline{\alpha}+e^{(\alpha q)x}\underline{\alpha q\underline{\varphi}}\right)\frac{x^n}{n!}\right)$$

$$=\left(e^{\alpha x}\underline{\alpha}+e^{(\alpha q)x}\underline{\varphi}\right)+\varepsilon\left(e^{\alpha x}\alpha\underline{\alpha}+e^{(\alpha q)x}\underline{\alpha q\underline{\varphi}}\right)$$

Thus, the proof is completed.

Theorem 3.3. (Catalan identities) For positive integers n,r such that $n>r$, then we have

$$\mathcal{T}f_{n+r}(\alpha,q)\,\mathcal{T}f_{n-r}(\alpha,q)-\mathcal{T}f_n^2(\alpha,q)=\alpha^{2n-1}q^{n-r}[r]_q\ \left(q^n-1\right)\ \underline{\alpha}\,\underline{\varphi}(1+\alpha q\varepsilon)$$

$$\mathcal{T}l_{n+r}(\alpha,q)\,\mathcal{T}l_{n-r}(\alpha,q)-\mathcal{T}l_n^2(\alpha,q)=\alpha^{2n}q^n(q-1)([-r]_q+[r]_q)\underline{\alpha}\,\underline{\varphi}(1+\alpha q\varepsilon).$$

Proof. By using (2), (3) and (7), we obtain

$$\mathcal{T}f_{n+r}(\alpha,q)\,\mathcal{T}f_{n-r}(\alpha,q)-\mathcal{T}f_n^2(\alpha,q)$$
$$=\left(\frac{\alpha^{n+r}\underline{\alpha}-(\alpha q)^{n+r}\underline{\varphi}}{\alpha-\alpha q}\right)\left(\frac{\alpha^{n-r}\underline{\alpha}-(\alpha q)^{n-r}\underline{\varphi}}{\alpha-\alpha q}\right)-\left(\frac{\alpha^{n}\underline{\alpha}-(\alpha q)^{n}\underline{\varphi}}{\alpha-\alpha q}\right)^2$$

$$\varepsilon\left(\left(\frac{\alpha^{n+r+1}\underline{\alpha}-(\alpha q)^{n+r+1}\underline{\varphi}}{\alpha-\alpha q}\right)\left(\frac{\alpha^{n-r+1}\underline{\alpha}-(\alpha q)^{n-r+1}\underline{\varphi}}{\alpha-\alpha q}\right)-\left(\frac{\alpha^{n+1}\underline{\alpha}-(\alpha q)^{n+1}\underline{\varphi}}{\alpha-\alpha q}\right)^2\right)$$

$$=\frac{\alpha^{2n-1}q^n(2-q^{-r}-q^r)\underline{\alpha}\underline{\varphi}}{\alpha-\alpha q}+\varepsilon\left(\frac{\alpha^{2n+1}q^{n+1}(2-q^{-r}-q^r)\underline{\alpha}\underline{\varphi}}{\alpha-\alpha q}\right)$$

$$=\frac{\alpha^{2n-1}q^n(1-q^{-r}+1-q^r)\underline{\alpha}\underline{\varphi}}{\alpha-\alpha q}+\varepsilon\left(\frac{\alpha^{2n+1}q^{n+1}(1-q^{-r}+1-q^r)\underline{\alpha}\underline{\varphi}}{\alpha-\alpha q}\right)$$

$$=\alpha^{2n-1}q^n([-r]_q+[r]_q)\underline{\alpha}\ \underline{\varphi}(1+\alpha q\varepsilon)$$

$$=\alpha^{2n-1}q^n\left(\frac{1-q^{-r}}{1-q}+\frac{1-q^{-r}}{1-q}\right)\underline{\alpha}\ \underline{\varphi}(1+\alpha q\varepsilon)$$

$$=\alpha^{2n-1}q^{n-r}[r]_q\ \ (q^r-1)\ \ \underline{\alpha}\ \underline{\varphi}(1+\alpha q\varepsilon).$$

Similarly we can get the result for q-Lucas dual tessarine number sequences.

Theorem 3.4. (Cassini identities) For $n\ \geq\ 1$, we have

$$\mathcal{T}f_{n+1}(\alpha,q)\,\mathcal{T}f_{n-1}(\alpha,q)-\mathcal{T}f_n^2(\alpha,q)=\alpha^{2n-1}q^{n-1}\ \ (q-1)\ \ \underline{\alpha}\ \underline{\varphi}(1+\alpha q\varepsilon)$$

$$\mathcal{T}l_{n+1}(\alpha,q)\mathcal{T}l_{n-1}(\alpha,q)-\mathcal{T}l_n^2(\alpha,q)=\alpha^{2n}q^{n-1}(q-1)^2\underline{\alpha}\ \underline{\varphi}(1+\alpha q\varepsilon).$$

Theorem 3.5. (d'Ocagne identities) For positive integer n and m, we have

$$\mathcal{T}f_m(\alpha,q)\mathcal{T}f_{n+1}(\alpha,q)-\mathcal{T}f_n(\alpha,q)\mathcal{T}f_{m+1}(\alpha,q)=\alpha^{m+n-1}\ \underline{\alpha\varphi}\big([m]_q-[n]_q\big)\big(1+\alpha\varepsilon[2]_q\big)$$

$$\begin{aligned}\mathcal{T}l_m(\alpha,q)\mathcal{T}l_{n+1}(\alpha,q)-\mathcal{T}l_n(\alpha,q)\mathcal{T}l_{m+1}(\alpha,q)&\\ =\alpha^{m+n+1}\ \underline{\alpha\varphi}(q-1)^2\big([n]_q-[m]_q\big)\big(1+\alpha\varepsilon[2]_q\big).&\end{aligned}$$

Proof. Using (2), (3) and (6), we obtain

$$\begin{aligned}\mathcal{T}f_m(\alpha,q)\mathcal{T}f_{n+1}(\alpha,q)-\mathcal{T}f_n(\alpha,q)\mathcal{T}f_{m+1}(\alpha,q)&\\ =\left(\alpha^{m-1}[m]_q\underline{\alpha}+(\alpha q)^m\underline{\beta}\right)\left(\alpha^n[n+1]_q\underline{\alpha}+(\alpha q)^{n+1}\underline{\beta}\right)&\\ -\left(\alpha^{n-1}[n]_q\underline{\alpha}+(\alpha q)^n\underline{\beta}\right)\left(\alpha^m[m+1]_q\underline{\alpha}+(\alpha q)^{m+1}\underline{\beta}\right)&\end{aligned}$$

$$\varepsilon\Big(\big(\alpha^m[m+1]_q\underline{\alpha}+(\alpha q)^{m+1}\underline{\beta}\big)\big(\alpha^{n+1}[n+2]_q\underline{\alpha}+(\alpha q)^{n+2}\underline{\beta}\big)$$

$$-\big(\alpha^n[n+1]_q\underline{\alpha}+(\alpha q)^{n+1}\underline{\beta}\big)\big(\alpha^{m+1}[m+2]_q\underline{\alpha}+(\alpha q)^{m+2}\underline{\beta}\big)\Big)$$

If we do some calculations, we get

$$\begin{aligned}\mathcal{T}f_m(\alpha,q)\mathcal{T}f_{n+1}(\alpha,q)&\\ &-\mathcal{T}f_n(\alpha,q)\mathcal{T}f_{m+1}(\alpha,q)\\ &=\alpha^{m+n-1}\,\underline{\alpha\varphi}\big([m]_q-[n]_q\big)\big(1+\alpha\varepsilon[2]_q\big).\end{aligned}$$

For the proof of q-Lucas dual tessarine number sequences, we use (2), (3) and (7) and get the result easily.

Definition 3.2. For complex polynomials $h(t)$ and $g(t)$, the q-Fibonacci dual polynomials $\tilde{F}_{q,n}(t)$ and q-Lucas dual polynomials $\tilde{L}_{q,n}(t)$are defined as follows:

$$\begin{cases}\tilde{F}_{q,n}(t)=h(t)\,(F_{q,n-1}(t)+\varepsilon F_{q,n}(t))-g(t)(F_{q,n-2}(t)+\varepsilon F_{q,n-1}(t))\\ \tilde{L}_{q,n}(t)=h(t)\,(L_{q,n-1}(t)+\varepsilon L_{q,n}(t))-g(t)(L_{q,n-2}(t)+\varepsilon L_{q,n-1}(t)).\end{cases}\qquad(9)$$

Here, $F_{q,0}(t)=0, F_{q,1}(t)=1, L_{q,0}(t)=2$ and $L_{q,1}(t)=h(t)$, respectively. Classify the q-polynomials $\tilde{F}_{q,n}(t)$ and $\tilde{L}_{q,n}(t)$ according to the $h(t)$ and $g(t)$ values, respectively.

i. Assume that $h(t)=aq+1$ and $g(t)=a^2q$ are constant polynomials. In this case, we can write as follows:

$$\begin{cases}\tilde{F}_{q,n}(t)=(aq+1)(F_{q,n-1}(t)+\varepsilon F_{q,n}(t))-a^2q(F_{q,n-2}(t)+\varepsilon F_{q,n-1}(t))\\ \tilde{L}_{q,n}(t)=(aq+1)(L_{q,n-1}(t)+\varepsilon L_{q,n}(t))-a^2q(L_{q,n-2}(t)+\varepsilon L_{q,n-1}(t)).\end{cases}$$

ii. Assume that $h(t)=\lambda(s)$ and $g(t)=-1$ are not constant polynomials. For this case, we obtain the following equality:

$$\begin{cases}\tilde{F}_{q,n}(t)=\lambda(s)(F_{q,n-1}(t)+\varepsilon F_{q,n}(t))+(F_{q,n-2}(t)+\varepsilon F_{q,n-1}(t))\\ \tilde{L}_{q,n}(t)=\lambda(s)(L_{q,n-1}(t)+\varepsilon L_{q,n}(t))+(L_{q,n-2}(t)+\varepsilon L_{q,n-1}(t)).\end{cases}$$

Roots of $r^2-h(t)r-1=0$ in (9) are

$$\alpha(r)=\frac{h(t)+\sqrt{h^2(t)+4}}{2}$$

$$\beta(r)=\frac{h(t)-\sqrt{h^2(t)+4}}{2}.$$

Then, the Binet formulas for q-dual polynomials $\tilde{F}_{q,n}(t)$ and $\tilde{L}_{q,n}(t)$ are

$$\tilde{F}_{q,n}(t)=\frac{\alpha(r)^n-\beta(r)^n}{\alpha(r)-\beta(r)}+\varepsilon\frac{\alpha(r)^{n+1}-\beta(r)^{n+1}}{\alpha(r)-\beta(r)}$$

and

$$\tilde{L}_{q,n}(t)=\alpha(r)^n+\beta(r)^n+\varepsilon(\alpha(r)^{n+1}+\beta(r)^{n+1}).$$

Definition 3.3. The q-Fibonacci dual tessarine polynomial sequences $A(t)$ and the q-Lucas polynomial sequences $B_{q,n}(t)$ are defined by the recurrence relation

$$A(t)=\tilde{F}_{q,n}(t)+\tilde{F}_{q,n+1}(t)i_1+\tilde{F}_{q,n+2}(t)i_2+\tilde{F}_{q,n+3}(t)i_3$$

$$B_{q,n}(t)=\tilde{L}_{q,n}(t)+\tilde{L}_{q,n+1}(t)i_1+\tilde{L}_{q,n+2}(t)i_2+\tilde{L}_{q,n+3}(t)i_3.$$

The initial conditions of the $\gamma_{q,n}(t)$ and $\delta_{q,n}(t)$ are

$$A_{q,0}(t)=\tilde{F}_{q,0}(t)+\tilde{F}_{q,1}(t)i_1+\tilde{F}_{q,2}(t)i_2+\tilde{F}_{q,3}(t)i_3$$

$$=i_1+h(t)i_2+\big(h(t)^2-g(t)\big)i_3,$$

$$A_{q,1}(t)=\tilde{F}_{q,1}(t)+\tilde{F}_{q,2}(t)i_1+\tilde{F}_{q,3}(t)i_2+\tilde{F}_{q,4}(t)i_3$$

$$=1+h(t)i_1+\big(h(t)^2-g(t)\big)i_2+\big(h(t)^3-2h(t)g(t)\big),$$

$$B_{q,0}(t)=\tilde{L}_{q,0}(t)+\tilde{L}_{q,1}(t)i_1+\tilde{L}_{q,2}(t)i_2+\tilde{L}_{q,3}(t)i_3.$$

$$=2+h(t)i_1+\big(h(t)^2-2g(t)\big)i_2+\big(h(t)^3-3h(t)g(t)\big)i_3$$

nd

$$B_{q,1}(t)=\tilde{L}_{q1}(t)+\tilde{L}_{q,2}(t)i_1+\tilde{L}_{q,3}(t)i_2+\tilde{L}_{q,4}(t)i_3.$$

$$=h(t)+\left(h(t)^2-2g(t)\right)i_1+\left(h(t)^3-3h(t)g(t)\right)i_2$$

$$+(h(t)^4-4h(t)^2g(t)-2g(t)^2)i_3$$

where i_1, i_2 and i_3 are the imaginary units satisfies the multiplication rule in (1).

Theorem 3.7. The Binet-like formulas of the q-Fibonacci dual tessarine polynomial $\gamma_{q,n}(t)$ and q-Lucasdual tessarine polynomial $\delta_{q,n}(t)$ are

$$A_{q,n}(t)=\frac{\alpha(t)^n\underline{\alpha}(t)-\beta(t)^n\underline{\beta}(t)}{\alpha(t)-\beta(t)}+\varepsilon\frac{\alpha(t)^n\underline{\alpha}(t)-\beta(t)^n\underline{\beta}(t)}{\alpha(t)-\beta(t)}$$

and

$$B_{q,n}(t)=\alpha(t)^n\underline{\alpha}(t)+\beta(t)^n\underline{\beta}(t)+\varepsilon(\,\alpha(t)^n\underline{\alpha}(t)+\beta(t)^n\underline{\beta}(t))$$

Here,

$$\underline{\alpha}(t)=1+\alpha(t)i_1+\alpha(t)^2i_2+\alpha(t)^3i_3$$

$$\underline{\beta}(t)=1+\beta(t)i_1+\beta(t)^2i_2+\beta(t)^3i_3.$$

Proof. The proof can be done easily by using Binet-like formulas of q-Fibonacci dual tessarine polynomial sequences and q-Lucas dual tessarine polynomial sequences.

Definition 3.4. (Kac & Cheung, 2002). Suppose that $p(t)$ is an arbitrary function. Its q-derivative operator is given by

$$d_qp(t)=p(qt)-p(t).$$

Note that in particular $d_q(t)=(q-1)t$,

$$\lim_{q\to 1} D_q p(t) = \lim_{q\to 1}\frac{p(qt)-p(t)}{(q-1)t} = \frac{dp(t)}{dt} \tag{10}$$

where $q \neq 1$.

Definition 3.5. The $n^{th}q$-Fibonacci dual tessarine and q-Lucas dual tessarine function sequences are defined as follows:

$$A_{q,n}(t) = \tilde{F}_{q,n}(t) + \tilde{F}_{q,n+1}(t)i_1 + \tilde{F}_{q,n+2}(t)i_2 + \tilde{F}_{q,n+3}(t)i_3$$

and

$$B_{q,n}(t) = \tilde{L}_{q,n}(t) + \tilde{L}_{q,n+1}(t)i_1 + \tilde{L}_{q,n+2}(t)i_2 + \tilde{L}_{q,n+3}(t)i_3,$$

respectively. Where $\tilde{F}_{q,n}(t)$ and $\tilde{L}_{q,n}(t)$ are the n^{th} q-Fibonacci dual function and q-Lucas dual functions and i_1, i_2 and i_3 are the imaginary units satisfy rules in (1).

The q-derivative of $A_{q,n}(t)$ and $B_{q,n}(t)$ is defined as:

$$\begin{aligned} D_q A_{q,n}(t) = {} & D_q\tilde{F}_{q,n}(t) + D_q\tilde{F}_{q,n+1}(t)i_1 + D_q\tilde{F}_{q,n+2}(t)i_2 \\ & + D_q\tilde{F}_{q,n+3}(t)i_3 \end{aligned}$$

and

$$D_q B_{q,n}(t) = D_q\tilde{L}_{q,n}(t) + D_q\tilde{L}_{q,n+1}(t)i_1 + D_q\tilde{L}_{q,n+2}(t)i_2 + \tilde{L}_{q,n+3}(t)i_3$$

where $D_q\tilde{F}_{q,n}(t)$ means the derivative of $\tilde{F}_{q,n}(t)$.

Example 3.1. For any integer n, if $\mathcal{F}_{q,n}(t) = (t-a)^n$,then

$$D_q\tilde{F}_{q,n}(t) = [n]_q\tilde{F}_{q,n}(t)$$

Proof. From (10), compute q-derivative of the function sequences $\mathcal{F}_{q,n}(t)$,

$$D_q\tilde{F}_{q,n}(t) \quad = \frac{\left(q(t-a)\right)^n-(t-a)^n}{(q-1)(t-a)} + \varepsilon\frac{\left(q(t-a)\right)^{n+1}-(t-a)^{n+1}}{(q-1)(t-a)}$$

$$= \frac{q^{n}-1}{q-1}(t-a)^{n-1} + \varepsilon \frac{q^{n+1}-1}{q-1}(t-a)^{n}$$
$$= [n]_q \mathcal{F}_{q,n-1}(t) + \ \varepsilon [n+1]_q \mathcal{F}_{q,n}(t)$$

and from above example the derivative of the n^{th} q-Fibonacci dual tessarine function sequences is

$$D_q A_{\mathrm{q,n}}(t) = [n]_q \mathcal{F}_{q,n-1}(t) + [n+1]_q \mathcal{F}_{q,n}(t) i_1 + [n+2]_q \mathcal{F}_{q,n+1}(t) i_2 + [n+3]_q \mathcal{F}_{q,n+2}(t) i_3$$

$$\varepsilon([n+1]_q \mathcal{F}_{q,n}(t) + [n+2]_q \mathcal{F}_{q,n+1}(t) i_1 + [n+3]_q \mathcal{F}_{q,n+2}(t) i_2 + [n+4]_q \mathcal{F}_{q,n+3}(t) i_3).$$

4. CONCLUSION

In this work, we define q-tessarine number sequences using notations from quantum calculus. Several fundamental are derived identities including Binet-like formulas, exponential generating functions, and Catalan-like, Cassini-like, and d'Ocagne-like identities for these numbers. Additionally, we introduce dual tessarine polynomial and dual function sequences,. We then present various properties and identities for these polynomials and function sequences. In the future, researchers may explore additional identities of dual tessarine number sequences within the framework of quantum calculus.

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Chapter 5

SECONDARY METABOLITES (BIOLOGICALLY ACTIVE SUBSTANCES) IN MYXOGASTRIA I: CARBOHYDRATES AND THEIR DERIVATIVES

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Introduction:

Myxomycetes (plasmodial slime molds, or myxogastrids) are phagotrophic amoeboid eukaryotes in the Eumycetozoa, in phylum Amoebozoa. Eumycetozoa is includes Myxogastria, Dictyostelia, and Protostelia. Slime molds are divided into two groups: acellular slime molds (Myxogastria and Protostelia) and cellular slime molds (Dictyostelium) (Willey et al., 2014). Members of the group are so small that it is almost impossible to observe them directly in the area. These organisms are cultured in the laboratory with moist chamber culture from a variety of plant and animal organic materials brought from the field. They feed on bacteria, protozoa, yeasts, nematodes, and other small organisms commonly found in decaying or living organic matter. They engulf and digest these whole by phagocytosis (Stephenson and Stempen, 1994; Ergül and Akgül, 2011).

Myxogastria are mostly common in terrestrial ecosystems and thrive in habitats rich in plants and animal decaying materiala (Paul et al., 2024). In the past, Myxogastria were classified plant, animal, fungi and protista. They are classified as Fungi because their fascinating generative structures resemble those of mushrooms and because they live in the ecological conditions that mushrooms require. They play an important ecological role by acting as prey by capturing and feeding on a variety of microorganisms (Baba and Sevindik, 2018). Myxogastria (Myxomycetes) are the acellular plasmodial slime molds and are usually characterized by prominent sporophores. Most slime molds are very small and microscopic during most of their life cycle. Some members of Myxogastria have macroscopic plasmodium and sporophores that can be seen with the naked eye (Stephenson and Rojas, 2017). Myxomycetes thrive on organic materials, particularly those prone to decay, and in warm, moist environments. In this process, they accumulate different levels and types of primary and secondary metabolites depending on the food content they phagocytose (Baba et al., 2020).

Myxomycetes are protists that have two stages in their life cycle: vegetative and generative stages. In the first stage, they behave like protozoa (amoeba) and in the second stage, they behave like fungi. In the protozoan stage, they feed by ingesting food particles and other microbes. After germination, the spores develop into myxamoeba in humid conditions or into myxoflagellates, which are flagellated swarmcells when exposed to higher humidity. Under environmental stress condition, myxamoeba and myxoflagellated can develop microcysts and struggle to alive. Under favorable conditions, they revert to their unicellular form. They reproduce sexually and produce plasmodium. Under favorable conditions, the plasmodium feeds, grows, develops, and differentiates into spore-producing fruiting bodies. If the plasmodium is exposed to prolonged environmental stress, it forms a sclerotium. When conditions return to normal, the sclerotium forms a plasmodium and then one or more fruiting bodies. Dispersal and germination of the spores produce new myxoamoeba or myxoflagellates, and so the cycle continues (Ergül, et al., 2016; Baba and Sevindik, 2024).

There are two types of metabolites in living things; Primary metabolites are found in all living things, perform nutrition, growth, development and reproduction activities, and play a role in all kinds of metabolic activities. Primary metabolites are nucleic acids, proteins, carbohydrates and fats. Secondary metabolites are generally known in low concentrations and as small compounds. Sometimes it is difficult to distinguish primary and secondary metabolites. For example, terpenoids are considered both primary and secondary metabolites. Secondary metabolites are not absolutely necessary for life, but they contribute to the survival process of the species. Secondary metabolite groups also serve as markers for chemotaxonomy. Secondary metabolites are synthesized as a defense mechanism when a living being is exposed to any stress factor. There are many secondary metabolites used chemically, especially as medicines, flavors, fragrances, pesticides and dyes, and therefore have great economic value (Bakır, 2020).

Myxogastria or Mxomycetes, are model organisms that are investigated and used in experiments with all stages of vegetative and generative stages. Myxogastria contain different bioactive compounds in all known developmental stages such as plasmodium, fruit body, spores, myxamoeba, myxoflagellate, microcyst, sclerotium in their complex and multistage life cycle. Myxogastria, with its fruit body size of 50-500 µm, makes it difficult to collect sufficient biomass for chemical analyses (Keller and Everhart, 2010). However, it also contains a potentially rich bioactive compound with the metabolites it accumulates in different developmental stages (Akgül et al., 2021).

Recently, with the increasing interest in natural bioactive substances, it has been thought that plants, animals, fungi and microorganisms such as slime molds may be good sources of natural compounds with bioactivity (Eraslan et al., 2021; Bal et al., 2022). Some of these molecules are microbial bioactive substances and have been shown to have antioxidant, cytotoxic and antimicrobial properties (Takafori, 2021). However, obtaining sufficient sample material to study the bioactive compounds of myxomycetes is difficult due to the very small fruiting bodies and under laboratory conditions due to the slow growth rate of their plasmodia.

There are numerous studies on secondary metabolites of plants, fungi, microorganisms and myxomycetes in the world (Akgül et al., 2021). Having both fungal and protozoan characteristics makes Myxomycetes an unusual group of Protists. However, biochemical research on the bioactive substances of myxomycetes is still quite insufficient in Türkiye. Sevindik et al. (2018) showed that *Physarum album* (Bull.) Chevall. has antioxidant and antimicrobial properties. Baba et al. (2020) examined the antioxidant potential, oxidant potential, oxidative stress index, antimicrobial activities and elemental contents of 6 myxomycete species (*Symphytocarpus amaurochaetoides* Nann.-Bremek., *Lindbladia tubulina* Fr., *Fuligo septica* (L.) FH Wigg., *Stemonitis fusca* Roth, *Tubifera ferruginosa* (Batsch) JF Gmel. and *Lycogala epidendrum* L. Fr.). As a result, it was determined that myxomycetes can be used as natural agents in antioxidant and antimicrobial drug design.

Materials and Methods:

Natural bioactiv secondary metabolites have played an important role in drug discovery, nutrition, and many industrial and engineering fields for the treatment of various human and animal diseases. Fungi, plants, animals and microorganisms especially bacteria are important organisms with secondary metabolism. Prokaryotic and eukaryotic microorganisms have provided a wide range of drugs, starting with the discovery of penicillin. However, the vast majority of microorganisms still await discovery as potential sources of new compounds. To date, approximately 500,000 secondary metabolites have been identified. Of these, approximately 100,000 natural products are obtained animals, 350,000 natural products from plants and 70,000 natural products obtained from microorganisms. Approximately 33,500 bioactive microbial metabolites have been identified. Of these microbial metabolites, approximately 12.5% (4,200) are metabolites of unicellular bacteria and cyanobacteria, 41% (13,700) are products of Actinomycete fermentations and approximately 47% (15,600) are of fungal origin (Nett et al., 2009; Berdy, 2012). The rate of discovery of new secondary metabolites, microbial natural products, has accelerated significantly in the last two decades (Bills and Gloer, 2016).

The types of bioactivity of secondary microbial metabolites include: Antimicrobial activity (Antibacterial, Antifungal, Antiprotozoal, Chemotherapeutic activity, and Antiviral), Pharmacological Activity, Biochemical activity, Other (antagonistic, regulatory, antiinflammatory), Agricultural Activity (Pesticide, Herbicide, Insecticide, Feed additive, preservative), Other Activities Microbial regulators, Biophysical effects (Berdy, 2005).

According to Dembitsky et al (2005), approximately 100 secondary metabolites obtained from myxogastria are present; lipids and their derivatives, alkaloids, amino acids, proteins and their derivatives, pigments, aromatic compounds, carbohydrate compounds and their derivatives, and terpenoid compounds. According to Pawłowicz et al. (2025), internationally recognized and chemical nomenclature standards (IUPAC) and to provide a robust, biosynthetically and structurally consistent framework, all known secondary metabolites in Myxomycetes include approximately 250 different chemicals in 8 main categories. This updated classification encompasses both discrete, well-characterized metabolites and molecules. All known chemicals are grouped as:

1. Carbohydrates and Their Derivatives,
2. Amino Acids, Peptides, and Proteins.
3. Lipids.
4. Polyphenols, Quinones, and Related Polyketides.
5. Pigments.
6. Alkaloids and Indole Derivatives.
7. Polyenes and Polyacetylenes.
8. Other Eumycetozoa-Specific Secondary Metabolites.

Results:

Carbohydrates and their derivatives are involved in most structural and metabolic processes throughout the Myxogastria life cycle, as in all other living things. Myxogastria produces both monosaccharides, disaccharides and polysaccharides in varying proportions depending on the vegetative and generative development period and environmental conditions. Most carbohydrates are seen in the structure of the mucosal components secreted extracellularly. They also constitute an important part of the complex protein-carbohydrate metabolism plasmodium and fruiting-body (Pawłowicz et al., 2025).

Two researchers, Simon and Henney (1970), showed that the slime secreted by *Physarum flavicomum* (Figure 1), *Physarum polycephalum* and *Physarum rigidum* was largely galactose-containing glycoproteins. Later studies showed that the exopolysaccharides present in the slime traces of *Physarum polycephalum* and *Physarella oblonga* could be rhamnose, galactose and glucose (Huynh et al., 2017). *Physarum polycephalum* has been found to produce an extracellular sulfated and phosphorylated β-D-galactan isolated from its nuclei (Horisberger et al., 1978).

Two new polypropionate lactone glycosides, named lycogalinosides A and B, were isolated from the sporophores of *Lycogala epidendrum* (Figure 2). Lycogalinoside A showed most important inhibitory activity against the growth of *Staphylococcus aureus* and *Bacillus subtilis*. Lycogalinoside B showed weaker biological activity but higher antifungal activity than lycogalinoside A. The results show that the chemical structures of both compounds are generally similar to chemicals produced by Streptomyces (Rezanka and Dvoráková, 2003). Lycogalinosides A and B, carbohydrate-based molecules isolated from the sporophore of *Lycogala epidendrum*, have been found to have inhibitory effects on Gram-positive bacteria (Wang et al., 2017; Li et al., 2020).

Figure 1. Physarum flavicomum

Figure 2. Lycogala epidendrum

Galactosamine, a polymer with solubility properties similar to the β1-4-linked glucosamine polymer (chitosan), is found in the spore walls of *Physarum polycephalum*. Spore walls have also been shown to contain approximately 2% protein, 1.4% phosphate, and approximately 15% melanin, which is similar to fungal melanin (McCormick et al.,1970).

Farr and Horisberger (1978) succeeded in isolating sulfated β-D-galactan from the cell nucleus of *Physarum polycephalum*. Murakami-Murofushi et al. (1990) reported that *Physarum polycephalum* plasmodium protein complexes contain mannose, glucosamine, fucose and glucose. Rezanka and Dvoráková (2003) identified secondary metabolites from *Lycogala epidendrum*, polypropionate lactone glycosides (lycogalinosides A and B), compounds bearing 2-deoxy-fucopyranosyl or gulopyranosyl moieties. The structural uniqueness of these metabolites and their inhibitory activity against the Gram-positive bacteria were later reported by many researchers and also by Dembitsky et al. (2005).

These data suggest that carbohydrates and their derivatives contribute to both extracellular matrices and intracellular structural elements. They also demonstrate the compositional complexity of carbohydrates in Myxogastria. Studies support that different types of carbohydrates produced at different points in the life cycle in Myxomycetes may play a role not only in nutrient storage and feeding, but also in for defense purposes, cellular communication and morphogenesis (Pawłowicz et al., 2025).

According to Kurodo et al. (1990), the analysis of membrane glycoproteins by isolation of the plasma membrane of *Physarum polycephalum* showed that the oligosaccharide chains in the glycoproteins are composed of mannose type oligosaccharides. Slime mold does not have a chitin containing cell wall.

Exopolysaccharides are microbial macromolecules, mostly composed of carbohydrate compounds, secreted into the environment by most microorganisms. Exopolysaccharides are centers of bacterial cell aggregation and serve as a nutrient source and protection against extreme environmental conditions (Nwodo et al., 2012). McCormick et al. (1970) showed that *Physarum polycephalum* plasmodium began to produce more Exopolysaccharides when the cells were transformed into spheres. They found that Exopolysaccharides was a sulfated galactose polymer with traces of rhamnose. Simon and Henney (1970) showed that Exopolysaccharides was a glycoprotein, a bioactive microbial molecule. Sperl (1990) found that Exopolysaccharides produced by *Physarum polycephalum* consisted of two galactans with different ratios of phosphorus and sulfur. Asgari and Henney (1977) showed in their study that Exopolysaccharides secreted by *Ph. flavicomum* plasmodium in liquid culture was mainly glycoprotein in structure. They also showed that this structure could inhibit Bacillus subtilis cell growth and division. It is known that microbial Exopolysaccharides have bioactive substances and that Myxomycete plasmodia also produce significant amounts of mucus. Bioactivities (antimicrobial, antioxidant and anticancer) of mucus traces and Exopolysaccharides samples isolated from *P. oblonga and Ph. polycephalum* were evaluated. Monosaccharide compositions of Exopolysaccharides produced by *Physarella oblonga* and *Physarum polycephalum* included glucose, galactose and rhamnose. Exopolysaccharides isolated from Plasmodium showed antimicrobial activity against *Staphylococcus aureus* and *Candida albicans*. However, *Candida albicans* was found to be the most sensitive to Exopolysaccharides of both species. The antimicrobial activities of these compounds (Exopolysaccharides) that are still in contact with Plasmodium can be explained by the possibility of protecting Plasmodium from biotic and abiotic factors (Huynh et al., 2017).

Physarum flavicomum Berk., like all other Myxomycetes, lacks a microplasmodia cell wall. However, microplasmodia are covered with a mucus layer that is constantly renewed and secreted continuously and accumulates in the liquid growth medium. Chemical analyses of the walls free of microcysts and microsclerotia revealed the presence of polysaccharides, lipids and proteins as the main components. The polysaccharide of the microcyst walls consists of galactosamine with lesser amounts of glucose, galactose and ribose. The polysaccharide of the microsclerotium walls is composed mainly of galactosamine with lesser amounts of glucose and galactose. The mucous layer of microplasmodia is composed of a polysaccharide containing galactose and protein (Henney and Chu, 1977).

Carbohydrates and derivatives obtained from Myxogastria are: β-D-galactan, Fucose, Galactose, Galacturonic acid, Glucosamine, Glucose, Glucuronic acid, Lycogalinoside A, Lycogalinoside B, Mannose, Rhamnose, Ribose Trehalose. Structures from which carbohydrates are obtained: Plasmodium, Slime trace, Fruiting body. Carbohydrate obtained species: *Lycogala epidendrum, Physarum flavicomun, Physarella oblonga, Physarum polycephalum, Physarum rigidum* (Pawłowicz et al., 2025).

Conclusions:

In this study, we investigated carbohydrate metabolites and their derivatives produced by Myxogastria. It is seen that these microbial bioactive compounds are closely related to the developmental stages of the organism (plasmodium, nutrition, spore production and fruitingbody) and environmental conditions (protection, defense, stress factors). It has been observed that they have various biological roles (antimicrobial, cytotoxic or signaling). Research on secondary metabolites, biochemical, genomic and ecological studies of Myxomycetes is not yet sufficient. It is also possible to discover more new secondary metabolites. As a result of these studies, biosynthetic pathways will be clarified and genetic or environmental factors that govern the production of compounds will be understood. The new metabolites obtained will contribute to the well-being of humanity.

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Chapter 6

RECENT DEVELOPMENTS IN PHYTONANOTECHNOLOGICAL STUDIES: A BIBLIOMETRIC ANALYSIS[1]

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1. İntroduction

Phytonanotechnology is a rapidly developing field of research that emerges from the use of bioactive molecules in plants in nanotechnology applications. This field offers a wide range of application potential from agriculture to medicine, from energy to the environment by promoting sustainable and environmentally friendly approaches (Rai et al., 2016; Singh et al., 2018). In particular, the development of green synthesis methods reduces the need for toxic chemicals and minimizes environmental impacts (Ahmed et al., 2020).

In recent years, research on plant-based nanoparticle synthesis has attracted both academic and industrial interest. These methods offer the advantage of less energy consumption and toxicity compared to traditional chemical and physical synthesis methods (Iravani, 2011). There are many studies in the literature in which metal and metal oxide nanoparticles such as silver, gold, zinc oxide and iron oxide are synthesized using plant extracts (Kumar and Yadav, 2009; Bar et al., 2009).

Phytonanotechnology has been defined and studied in various ways by researchers from different disciplines. Plant-based nanoparticle synthesis provides superiority over traditional methods with both environmental sensitivity and biocompatibility. For example, Shankar et al. (2004) showed that silver nanoparticles can be synthesized rapidly and efficiently using Azadirachta indica plant extract. Mukherjee et al. (2001) achieved successful results in the production of gold nanoparticles with Aloe vera. Phytonanomaterials have shown promising results in drug delivery, cancer treatment and antimicrobial applications. Kasthuri et al. (2009) stated that plant-based gold nanoparticles have biocompatible properties and can be used especially in cancer treatment. Nabikhan et al. (2010) emphasized the antibacterial effect of silver nanoparticles synthesized from plant extracts. Plant nanoparticles are used as yield enhancing agents in agriculture and as materials that reduce environmental pollution. Gade et al. (2010) showed that nanoparticles are effective in promoting plant growth and combating harmful organisms. In addition, plant-based nanoparticles are widely investigated in environmental applications such as heavy metal removal (Prasad et al., 2014).

In the literature, it is stated that plant-based nanoparticle synthesis has gained importance as an environmentally friendly method that does not use toxic chemicals. These studies are integrated into many sectors such as health, agriculture and environment with innovative approaches (Raghunandan et al., 2011). Bibliometric analyses reveal that studies in the field of phytonanotechnology have shown rapid growth in terms of both the number of publications and the variety of applications.

Bibliometric analyses are an important tool to understand the development of phytonanotechnology and to determine research trends in this field. This method provides a numerical and qualitative analysis of publications in the literature, determines the most active authors, journals and countries and provides valuable information for future research directions (Donthu et al., 2021). In this context, the present study aims to reveal the recent developments and research trends in the field of phytonanotechnology.

2. Materials and Methods

The study aims to analyze the thematic trends of phytonanotechnological research, the number of published articles, keywords, authors and journals, and to analyze scientific trends and research networks in this field. This section includes the creation of the database and the analysis of the visualization of scientific studies (VOSviewer).

2.1. Creating a Database

The first step is to create a database containing studies on phytonanotechnology. For this purpose, a comprehensive literature search string consisting of keywords related to phytonanotechnology was used. The search terms were selected based on the authors' field and area of expertise.

The search string used in this study is as follows: "Phytonanotechnology" AND "Green Synthesis" AND "Plant". In addition to being limited by "subject section" (title, keywords, and abstracts) to identify publications that mainly focus on phytonanotechnology, the search results were not limited by genres such as articles and books. Although this search could not retrieve all relevant publications, it did find publications where the researcher(s) focused on phytonanotechnology. The search was conducted on December 2, 2024, based on abstracts, keywords, and titles (English only) of research studies indexed since 2015. 19 studies were retrieved from the following Web of Science (WoS) databases: Science Citation Index Expand and Emerging Sources Citation Index. Twenty-one studies were retrieved from the Scopus database: Science Citation Index Expanded, Social Sciences Citation Index, Arts and Humanities Citation Index, and Emerging Sources Citation Index.

These databases were selected for two main reasons: (1) they are well known in academia for archiving quality peer-reviewed research; (2) software tools available for text mining and bibliometric analysis can only process bibliographic outputs produced by these databases.

The initial search results revealed some publications related to engineering and medical science information systems due to the shared terminology between these research fields. Therefore, irrelevant publications unrelated to phytonanotechnology were filtered from the database. Overall, 6 publications were removed from the database after careful review of abstracts, keywords, and titles by the authors. The final database contains 40 publications (Table 1).

Tablo 1. Search strategy and multi-faceted bibliometric analysis framework

Stages	**Details**
Determining Research Questions	- Defining the purpose and scope of the research - Creating key research questions
Selection of Databases	- Selecting appropriate databases (Web of Science, Scopus) - Determining data access methods
Creating a Search Strategy	- Determining keywords and synonyms (AND, OR, NOT) - Applying restrictions such as time frame, subject area, language and genre - Applying search formulas to databases
Data Collection	- Conducting a literature review - Downloading results in appropriate formats (e.g. .csv, .txt)
Data Preprocessing	- Removal of duplicate records - Correction of missing or incorrect data - Standardization of author names - Checking the accuracy of citation information
Bibliometric Analysis	- Analysis of Basic Indicators: - Number of publications (distribution by year) - Most cited studies - Most productive authors, journals and institutions - Network Analysis: - Author collaboration networks - Inter-institution collaboration networks - Term co-occurrence analyses - Citation Analysis: - Most cited authors, articles and journals - Creation of citation networks - Thematic Mapping: - Word co-occurrence analyses - Determination of topic clusters and thematic trends
Data Visualization	- Use of tools for visualization of analysis results: - VOSviewer: Co-occurrence, citation and author collaboration networks
Interpretation of Results	- Analyze findings and answer questions - Identify important trends, authors, and studies - Highlight gaps in the literature and future opportunities

2.2. Inclusion and Exclusion Criteria

The articles included in the study were selected according to the following criteria:

- Academic articles, journals and conference proceedings that deal with topics related to phytonanotechnology.

- Articles must include studies on original research, reviews and compilations.

- Only articles in English were included.

The excluded studies were in the following categories:

- Articles that were not directly related to the topic and only dealt with nanotechnology, plants and green synthesis.

- Studies that were outside the research topic and did not use phytonanotechnological methods or present data on their biomedical and environmental applications.

2.3. Data Analysis

The collected data were evaluated with the following methods for bibliometric analysis:

- Annual distribution of the number of articles: The annual distribution of the number of published articles was analyzed to examine the trends in phytonanotechnology research over time.

- Keyword analysis: The most frequently used keywords in the articles were determined and the relationship of these keywords with the research topics was revealed. The frequency of the keywords was accepted as an indicator of research trends in this field.

- Collaboration between authors and institutions: The collaboration between authors and research institutions was evaluated with geographical distribution and co-authorship analyses. The most cited authors and research institutions were determined.

- Citation analysis: Citation links were examined to determine the impact of specific articles and important studies in this field. The most cited articles were defined as important references for the development of the subject.

- Journal analysis: Important journals published on phytonanotechnology and the impact factors of these journals were taken into consideration. Trends among the articles published in these journals were examined to show the areas where research topics are concentrated.

2.4. Analysis Using VOSViewers

In the last few years, different visualization tools have been used for science mapping and bibliometric analysis (Cobo et. all., 2011). The main objectives of these visualization tools are to show the dynamic and complex relationships between fields, authors, journals, organizations, countries, and basic concepts of knowledge. In this study, VOSviewer, a widely used tool with a simple and easily interpretable graphical interface, was used to create bibliometric networks of authors, publications, journals, organizations, and countries (Sharifi, 2021). The maps were created according to the analysis of co-terminology, co-authorship, bibliographic linkage, and co-citation. In order to provide more accuracy in the analysis, a thesaurus file was created and adopted in this study (e.g., "Phytonanotechnology," "Phyto-nanotechnology," and "Phyto-nanotechnology" all refer to the same terminology and were combined as "Phytonanotechnology").

In addition to the co-occurrence analysis, bibliographic link analysis was conducted between countries and organizations to identify the most prominent organizations and countries conducting research in the field. Co-citation analysis was also used to identify the most important publications and show their relationships. The output of each of these analyses is a node and link graph network, where larger nodes and thicker links indicate higher importance of these components. The maps generated by VOSviewer are based on the modularity-based clustering method involving nodes and links. The node sizes indicate the frequency of evaluations, and the thickness of the links indicates the strength of the connections between the nodes. In addition, closely connected nodes form clusters, for example, in the case of term co-occurrence analysis, indicating thematic clusters.

3. Findings

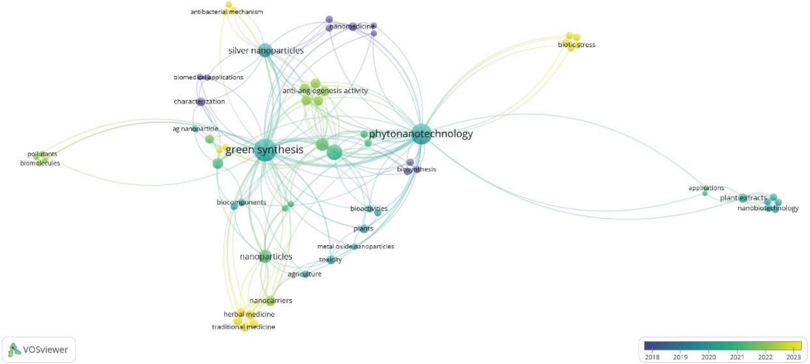
The results of the term co-occurrence analysis and bibliographic matching are presented in this section. The maps show the thematic density of research in the field of phytonanotechnology and the relationships between keywords. Key concepts in the visuals are classified according to their size and color: Node size: Represents the frequency of use of the keyword in publications. Node connections: Represent relationships between keywords. Color codes: Represent research trends over time.

3.1. Term Co-Occurrence Analysis (Descriptive Data)

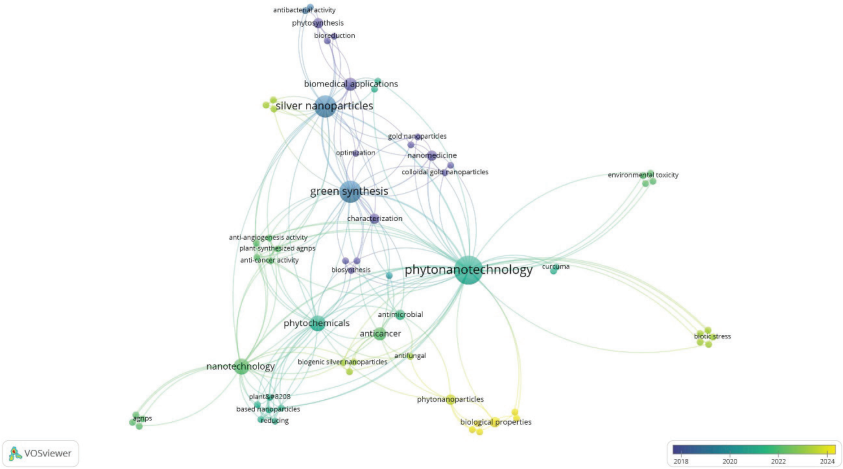
Term co-occurrence analyses were conducted to identify thematic clusters of the phytonanotechnology topic. This bibliographic method is useful for identifying key concepts and identified topics and can be used to define thematic clusters (Cobo et. all., 2011). Using the software allowed us to identify thematic clusters based on the strength of the connections between terms. The frequency of co-occurrence of terms shapes the clusters. This requires prior knowledge of the field, understanding of the evolution of navigation over time, and the use of advanced technological methods. The map of the VOSviewer analysis is shown in Figure 1. The node sizes are proportional to the number of terms. The frequency of co-occurrence of the 20 most frequent terms is presented in Table 1.

The most common research topics during the period 2015-2024 were "Green synthesis" (Scopus/n= 69, WOS/n=35), "Phytonanotechnology" (Scopus/n= 55, WOS/n=35), "Phytochemicals" (Scopus/n= 28), "Silver nanoparticles" (WOS/n=33) (Table 2). These topics also showed the highest values of the total connection strength. This suggests that these key terms were paid more attention by the authors. The terms "Green synthesis", "Phytonanotechnology", "Pyhtochemicals" and "Silver nanoparticles" showed a higher frequency of co-occurrence and appeared close to the boundaries of the clusters, indicating that these were cross-cutting terms with strong connections to different clusters and terms (Figure 1). The high values of the terms "Green synthesis", "Silver nanoparticles" and "Nanotechnology" indicate that Phytonanotechnology; It is investigated from the perspective of biotechnology, molecular biology, engineering, agriculture and biological sciences.

Figure 1 shows that clusters can be defined according to Scopus and WOS databases based on co-term occurrence analysis. According to the time scale in the lower right corner of the figures, the colors of the keywords correspond to a certain time period.



(Scopus)



(Web of Science)

Figure 1. Co-occurrence term map

In Scopus (Figure 1), purple and blue tones (2018-2020): Topics such as "Nanomedicine" and "biomedical applications" have been the focus of research in this period. Green tones (2021-2022): Topics such as "Green synthesis", "nanoparticles" and "biotic stress" have become popular in recent years. Yellow tones (2022-2023): Topics such as "Herbal medicine" and "biotic stress" stand out as important research areas for the future. "Phytonanotechnology" and "green synthesis": Green synthesis shows a strong relationship as environmentally friendly nanoparticle production methods in phytonanotechnological applications. "Silver nanoparticles" and “antibacterial mechanism”: The antibacterial properties of silver nanoparticles are one of the most researched biomedical applications in this field. “Plant extracts” and “nanobiotechnology”: Plant extracts have an important place as a natural and sustainable resource in nanotechnology. According to the data, the following topics are noteworthy: Environmentally Friendly Synthesis Methods: The themes of “Green synthesis” and “biocomponents” are seen to be on the rise. Biomedical Applications: The topics of “Nanomedicine” and “anticancer” emphasize the potential of phytonanotechnology in the health sector. Plant-Based Nanotechnology: Concepts such as “Plant extracts” and “nanobiotechnology” focus on the use of natural resources.

Table 2. Term co-validity analysis (top 20 most frequent terms)

Keywords	Scopus		Web Of Science		Keywords
	Events	Total Connection Power	Events	Total Connection Power	
Green synthesis	14	69	11	54	Phytonanotechnology
Phytonanotechnology	11	55	7	35	Green synthesis
Pyhtochemicals	5	28	7	33	Silver nanoparticles
Silver nanoparticles	4	22	4	26	Nanotechnology
Nanoparticles	4	21	4	26	Pyhtochemicals
Nanotechnology	3	18	3	13	Anticancer
Antimicrobial	3	13	3	12	Biomedical applications
Nanocarriers	2	12	1	9	Anti-angiogenesis activity
Anti-angiogenesis activity	1	9	1	9	Anti-cancer activity
Anti-cancer activity	1	9	1	9	Anti-microbial activity
Anti-microbial activity	1	9	1	9	Metallic nanoparticles
Metallic nanoparticles	1	9	2	9	Nanomedicine
Nanomedicine	2	9	1	9	Plant- synthesized agnps
Plant- synthesized agnps	1	9	2	9	Antimicrobial
Plants	2	9	1	8	Based nanoparticles
Toxicity	2	9	1	8	Capping agents
Anticancer	2	8	2	8	Characterization
Characterization	2	8	1	8	Green synthesis
Plant extracts	2	8	2	8	Pyhtonanoparticles
Herbal medicine	1	7	1	8	Plant extracts

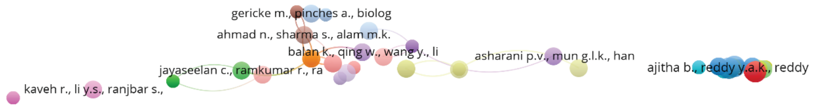
In WOS (Figure 1), purple and blue tones (2018-2020): It is observed that terms such as “Antibacterial activity”, “bioreduction” and “green synthesis" have attracted great attention in the past. Green and yellow tones (2021-2024): Terms such as "Biotic stress", "biological properties" and "environmental toxicity" show the new research directions of phytonanotechnology in recent years. The lines between the keywords show that these concepts are used together in the same studies. The strong connection between "silver nanoparticles" and "anticancer" reveals that silver nanoparticles are intensively researched for cancer treatment. Silver nanoparticles help minimize toxic effects by being synthesized from plant sources (Mittal et al., 2020). The close relationship between "green synthesis" and "biosynthesis" shows that biological methods are at the forefront for the production of nanoparticles from plant sources. Plant-derived nanoparticles are used to reduce environmental toxicity, increase soil fertility, and support plant growth under biotic stress conditions (Gole, et al., 2022). In recent years, studies in areas such as green synthesis, biomedical applications, and environmental sustainability have increased. Silver nanoparticles and phytochemicals play a leading role in the biomedical and environmental applications of phytonanotechnology.

3.2. Prominent Publications

Co-citation analysis was also used to identify the most important publications in this field. Figure 2 shows the analysis according to the references cited for at least 1 citation count (Figure 2).

According to the Scopus map:

Balan K. and Qing W. are in the center of the image. The works of these authors focus especially on nanotechnology and biological synthesis. Authors such as Qing W. have made important studies in nanoparticle production and applications in terms of environmental sustainability. The works of Gericke and Pinches, who have a relatively important position in the network, are on the understanding of biosynthesis mechanisms and various industrial applications of nanoparticles (Gericke & Pinches, 2006). In these studies, there is an emphasis on the sustainability of green synthesis and toxicity reduction. Asharani's works examine the biomedical applications and toxicological effects of silver nanoparticles (Asharani et al., 2008). These authors, located on the right side of the image, are notable for their studies focusing especially on the toxic effects of silver nanoparticles.



(Scopus)

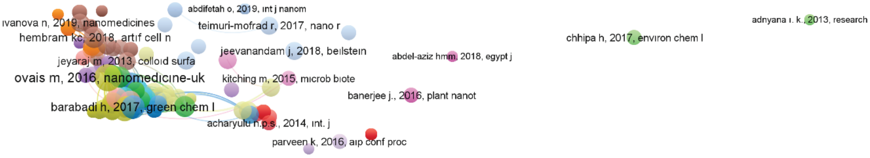


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Figure 2. Co-citation analysis based on cited references

Three main clusters can be identified based on the authors' areas of expertise. Pink Cluster (Kaveh R., Li Y.S., Ranjbar S.): These authors represent one of the more marginal groups in the field of nanotechnology and biosynthesis. Green Cluster (Jayaseelan C., Ramkumar R.): These authors stand out with their work focused on biocompatible nanoparticles and agricultural applications. The development of nanoparticles that support agricultural production is the main research area of this cluster (Jayaseelan et al., 2012). Blue and Red Cluster (Ajitha B., Reddy Y.A.K., Reddy): These authors are active in the synthesis and characterization of nanoparticles. Authors like Reddy are particularly interested in the optical and catalytic properties of silver and metal oxide nanoparticles (Ajitha et al., 2015).

According to the WOS map:

Ovais M. (2016), which is the largest node in the visual, emphasizes the applications of nanotechnology, especially in nanomedicine. The research of Ovais and his colleagues examines the synthetic and green synthesis routes of biocompatible nanoparticles, and stands out especially in biomedical applications such as cancer treatment (Ovais et al., 2016). The study of Barabadi H. (2017) addressed the sustainable and environmentally friendly production methods of nanoparticles within the scope of green chemistry. This study shows that silver and metal oxide nanoparticles are synthesized through green synthesis using plant extracts and biomolecules (Barabadi et al., 2017). Particularly, toxicity reduction and biomedical compatibility are important emphases in this study. The study of Hembram (2018), which has a dense connection network, was published in the journal Artificial Cells and addressed the relationship between nanotechnology and cell biology. The study focuses on the effects of nanoparticles on biological systems, drug delivery systems and biomedical applications (Hembram et al., 2018). Ivanova's (2019) study provides important contributions to the field of nanomedicine. It investigates the effects of nanotechnological solutions especially in antibacterial applications and drug delivery systems. Jeyaraj's (2013) study represents the early developments of nanotechnology. This study, published in the journal Colloids and Surfaces, addressed issues such as surface characterization of nanoparticles and colloidal stability.

Three main clusters can be determined according to the authors' areas of expertise. Purple Cluster: Studies on nanomedicine; It has received intensive citations especially between 2016-2019. Publications such as Ovais M. (2016) and Ivanova N. (2019) emphasize the role of nanotechnology in biomedical applications. Green Cluster: Green chemistry and sustainable synthesis studies are represented by researchers such as Barabadi H. (2017) and Chhipa H. (2017). Red and Yellow Clusters: Represent fewer but thematically diverse studies. Biological applications and nanoparticle characterization are at the forefront among these clusters.

In addition, it is seen in the visual that the studies published between 2016-2019 are dense. This period is the period when there was a significant growth and application diversity in nanotechnology research. 2013-2017: Older studies such as Adnyana I.K. (2013) and Jeyaraj M. (2013) are the main cited studies in the literature and are especially focused on colloid chemistry. New Trends: After 2017, especially green synthesis and nanomedicine studies are cited more (Barabadi et al., 2017).

3.3. Prominent Authors

A co-citation analysis using cited authors was conducted to identify the most influential authors in the phytonanotechnology literature. The most important authors with at least 1 citation are presented. The size of the nodes (dots) on the map represents the total number of citations to the authors' publications, while the color clusters represent the collaboration groups between the authors. The connections between the nodes reflect the strength of the collaborations (Figure 3).

According to the Scopus map:

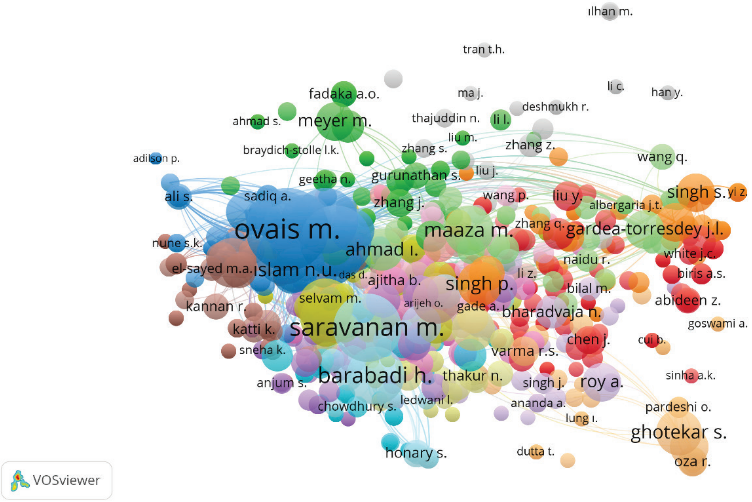
Ovais (2018) and Saravanan (2016) have the largest nodes and are located in a central position. This indicates that these authors have published influential publications with high citation numbers and contribute to a wide collaboration network. Ovais has undertaken widely cited studies, especially in the field of nanotechnology and biological nanoparticle synthesis (Ovais et al., 2018). Saravanan is known for his work on green synthesis methods and biomedical applications. She has made influential publications, especially on the antimicrobial properties of silver nanoparticles (Saravanan et al., 2016). Gardea-Torresdey J.L. also stands out as an important author on the map. She is known for her influential studies on plant-based nanoparticle synthesis and environmental applications. Gardea-Torresdey's studies emphasize the principles of green chemistry by focusing on the role of plants in biological nanoparticle synthesis (Gardea-Torresdey et al., 2003). Singh has an important position on the map with her contributions to the environmental and biomedical applications of nanotechnology. Singh has worked especially on the production of gold and silver nanoparticles by biosynthesis methods and examined the biological activities of these particles (Singh et al., 2015). Authors are grouped in certain color clusters on the map. These clusters indicate that the authors focus on different thematic research areas: Blue Cluster (Ovais, Islam, Ahmad): This cluster focuses on biological nanoparticle synthesis and nanotechnological applications, in particular, in cancer therapy. The work of Ovais and his team investigates the biocompatibility and biomedical potential of nanoparticles (Ovais et al., 2018). Red Cluster (Gardea-Torresdey J. L., Chen J., Bharadwaja N.): This cluster focuses on environmental applications and plant-based nanoparticle synthesis. In particular, the work of Gardea-Torresdey highlights the importance of nanoparticles for agricultural and environmental sustainability (Chen et al., 2014). Green Cluster (Maaza M., Meyer M., Zhang J.): This cluster works on materials science and the physical properties of nanomaterials. In particular, Maaza M. investigates the role of nanoparticles in optical and photonic applications (Maaza et al., 2015). Yellow Cluster (Saravanan M., Singh P., Bharadwaja N.): The yellow cluster focuses on biological and antimicrobial nanoparticles. Authors such as Singh P. and Saravanan M. examine the efficacy of nanoparticles against bacterial and fungal infections (Singh et al., 2015; Saravanan et al., 2016).

Authors with large nodes stand out as authors whose publications receive high citations: Ovais M. (nanotechnological biomedical applications), Gardea-Torresdey J.L. (environmental nanotechnology), Saravanan M. (antimicrobial nanoparticles).

According to the WOS map:

In the image, Barabadi (2019) has the largest node and is located in a central position. Barabadi is especially known for his work on nanotechnology, biosynthesis and biomedical applications. Barabadi et al. (2019) highlights the environmental and economic advantages of nanoparticle production via biosynthesis. Shankar and Khalil, in close collaboration with Barabadi, are at the center of the map. Shankar is particularly known for his work on the antimicrobial effects of silver nanoparticles. The work of Shankar et al. (2016) is an important publication examining the effectiveness of nanoparticles against bacterial and fungal infections. Khalil, on the other hand, focuses on nanoparticle synthesis and medical applications through biotechnological methods. Gurunathan (2018) is a significant contributor to the biomedical applications of nanotechnology. His work on the role of gold and silver nanoparticles in cancer treatment has been widely cited (Gurunathan et al., 2018).

Collaboration networks among authors are grouped into clusters, shown on the map with 4 different colors: Orange Cluster (Barabadi, H., Shankar, S.S., Khalil, A.T.): This cluster focuses specifically on biological nanoparticle synthesis and antimicrobial applications. Barabadi and Shankar emphasize the importance of biosynthesis methods for environmental sustainability (Barabadi et al., 2019). Green Cluster (Gurunathan, S., Hembram, K.C., Kumar, V.): The green cluster works on biomedical and medical applications of nanotechnology. Gurunathan has pioneered studies on the cytotoxic effects of nanoparticles on cancer cells.



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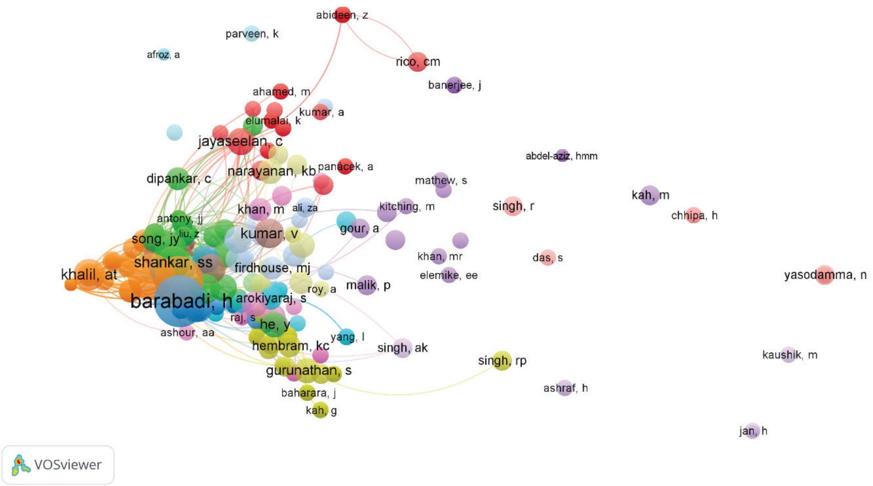

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Figure 3. Co-citation analysis by authors

4. Discussion And Conclusion

This article investigated the evolution and current trends of peer-reviewed phytonanotechnology. Using a bibliometric method, the geographical representation and temporal trends of research priority topics were revealed, providing a review of the most cited articles, authors, core journals, and research collaboration clusters. In general, the topic of phytonanotechnology has attracted attention across journals, sectors, and disciplines with a rapid growth rate. The core topics have clearly diversified, especially in the last decade, with new topics such as green synthesis and silver nanoparticles.

4.1. Theoretical implications

Although the subject of phytonanotechnology has attracted attention in the literature, there is a lack of information on the evolution and trends of studies covering green synthesis, plants and silver nanoparticles over time. This review aims to improve the understanding of the field of phytonanotechnology. This article provides a broad assessment of general trends in phytonanotechnology science. In particular, this assessment has allowed to track progress towards a better understanding of phytonanotechnology and its application areas. The main objective of this study is to provide an overview of the literature on the assessment of the subject of phytonanotechnology. The findings of the study show that a large number of studies have been published in the last decade and that there has been a rapid increase in the number of publications since 2015. Our analysis looked at the geographical distribution of knowledge contributions, co-authorship affiliations, tracked changes in research priority themes over time and examined the most influential journals, articles and authors underlying the literature. The knowledge mapping and analysis of the evolution of phytonanotechnology presented in this article is an attempt to create a universal language, provide a framework for managing and organizing the literature and offer suggestions for future work. This review aims to deepen the understanding of phytonanotechnology, which can serve as a resource for researchers and practitioners. The first publication recorded from this mapping review was published in 2015 and focused on the phytosynthesis of silver nanoparticles (Rajan et.al., 2015). The analysis shows that there were 39 publications in the following 9 years (2015-2024). The subject areas covered by this literature mapping have increased significantly over time. The results of this study show that despite a rapid increase in the number of publications over time, the phytonanotechnology literature is dominated by four countries (India, Pakistan, China, and Saudi Arabia).

4.2. Limitations

Although bibliometric analysis is considered an innovative method for visualizing and evaluating large amounts of data, the findings obtained should be interpreted carefully due to several limitations. Tools such as VOSviewer offer a highly effective solution for mapping and visualizing literature in the face of increasing numbers of academic publications. However, this does not mean that bibliometric analyses can completely replace a holistic and systematic review.

In this study, the scanning process was mostly carried out on article titles, abstracts, and keywords. In the future, literature mining focusing on full-text analyses and the use of advanced machine learning techniques can increase the depth and accuracy of the results obtained. It should be noted that in term co-occurrence analyses and thematic clustering, only the frequency of co-occurrence of terms is taken into account. Such analyses do not provide a comprehensive explanation of the relationships between terms and therefore should be interpreted with caution.

The bibliometric maps obtained within the scope of this study helped to reveal certain themes and trends. However, these findings should be considered as a starting point for a more in-depth analysis and should be supported by systematic reviews. Bibliometric analyses are quite effective in revealing the general appearance and structure of a research field; however, these methods are not sufficient on their own in terms of evaluating the quality of publications. In this context, conducting more detailed analyses is an inevitable necessity, especially to evaluate the quality of publications.

Another limitation of the study is that the main purpose of the study is to provide a general perspective. Especially when it comes to a complex and still developing research field such as phytonanotechnology, detailed and comprehensive assessments are needed. Bibliometric studies provide a framework that supports systematic reviews rather than replacing them. Therefore, the sub-topics discussed in the study should be addressed with more comprehensive and detailed analyses in the future. In summary, this study generally reveals the trends in the field, but emphasizes the need for more in-depth studies.

4.3. Conclusion

Phytonanotechnology has shown significant scientific development in recent years as an environmentally friendly, sustainable and multidisciplinary field. This bibliometric study reveals the growth trend, interdisciplinary interactions and future potential of research in the field of phytonanotechnology.

The findings of the study have shown that phytonanotechnology offers a strong innovative capacity, especially in fields such as medicine, agriculture and environmental engineering. The biocompatible and environmentally friendly properties of plant-derived nanoparticles stand out as sustainable alternatives to replace toxic chemicals. In medical applications, cancer treatment and antimicrobial solutions, and in agricultural applications, pesticide and fertilizer development have been the main focal points in this field.

The results of the bibliometric analysis show that academic interest in phytonanotechnology has increased rapidly in recent years and interdisciplinary collaborations have become widespread. The increase in the number of publications reveals that international collaborations are strengthening and more investments are being made in this field. In addition, the most cited publications and influential authors determine the important focal points of knowledge production in the field of phytonanotechnology.

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