CHEMIRESISTIVE SENSORS APPLICATIONS OF BIO-POLYMER NANOCOMPOSITES

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Abstract

The excessive reliance on petroleum chemicals in the manufacture of polymers is one of the main issues with economic and environmental sustainability. With an emphasis on medical and environmental issues, this article provides an overview of the current state of knowledge on the characteristics, compounding techniques, and uses of biopolymers paired with biosensors. Consequently, this article is focused on polymer materials that are ecologically beneficial. The paper provides a summary of the current state of knowledge about the characteristics, compounding techniques, and uses of biopolymers mixed with biosensors, with an emphasis on medical and environmental issues. The study discusses both potential and the existing level of knowledge. The article demonstrates the widespread interest in biopolymers created from renewable basic resources in both research and business. These materials provide unique combinations of characteristics for brand-new applications in addition to replacing conventional polymers in numerous applications. Because biopolymer-based composite materials may decay when exposed to environmental variables, they are thought to be preferable to conventional non-biodegradable materials. The research emphasises the use of polymers and nanomaterials in the manufacture of chemical sensors, which, owing to their biocompatibility and sensitivity, enable their use in environmental or medicinal applications. The analysis of current research in the area of biopolymer-sensor composites is the main goal of this study.

Keywords: *Biopolymers, Biocomposite Polymers, Chemiresistive sensors, and Environmental and Medical Applications*

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Introduction

The use of biosensors as diagnostic instruments is widespread, including in the fields of health, the environment, and packaging [1–5]. It is interesting that sensors may be used with biopolymers and natural polymers, which are sustainable and natural alternatives to polymers derived from petroleum. Chemical and biological components can interact with monitoring devices called biosensors to produce useful information [1]. High sensitivity, selectivity, on-time response, stability, reversibility, cheap cost, and ease of use are characteristics of modern sensors. Their major benefit is the prompt response to the monitored factor's existence, which enables prompt intervention. The advancement of chemistry and materials engineering opens up numerous potentials for the creation of novel solutions, whose implementation in daily life represents a turning point for the preservation of human health, the environment, food waste, agriculture, and many other fields [1]. Several of the natural polymers that are frequently employed in combination with sensors include chitosan, alginate, cellulose, and starch. The features of biopolymers, such as their capacity to gather and aggregate analytes on sensor surfaces, and the flexibility to produce and use a variety of forms, lead to their vast range of applications. Every year, more and more scientists are becoming interested in the application of biosensors and biopolymers in a variety of scientific domains. The use of sensors in environmental research and medicine has been discussed in several scientific studies. The rising body of scientific research demonstrates both the immense promise of this field and, more importantly, the pressing necessity for creating cutting-edge tools for tracking certain characteristics. The foundational and implementational works both make significant contributions to this discipline and serve as a guide for the discovery of novel ideas. Several of the natural polymers that are frequently employed in combination with sensors include chitosan, alginate, cellulose, and starch. The features of biopolymers, including as their capacity to aggregate analytes on sensor surfaces and the ability to be produced and used in a variety of forms (film, sponge, hydrogel), lead to their vast range of applications. The foundational and implementational works both make significant contributions to this discipline and serve as a guide for the quest for novel ideas. This study provides a summary of the current understanding of the characteristics, linking techniques, and uses of biopolymers in conjunction with biosensors, with a focus on the medical and environmental aspects. Future views as well as the existing level of knowledge were given.

Composites comprised of biopolymers

Both in today's business and the biological world, polymers play a significant role. Many naturally occurring polymers, including proteins and nucleic acids, transmit essential biological information, whereas other polymers, like polysaccharides, provide energy for cellular processes and act as supportive components in living structures [1]. Numerous applications, including food packaging, cosmetics and medicine, biomimicking, actuators, tissue engineering, sensors, and ultrasound imaging, can make use of biopolymers [6]. Research on biodegradable polymers and their composites has significantly increased in recent years. This phenomena is linked to issues with the management of discarded non-biodegradable plastics and the steady depletion of crude oil reserves. Materials called biopolymers have potential uses across the board in the economy.

If at least one component is biobased or biodegradable, polymer composites are considered biocomposites. Although the words "biopolymer" and "biodegradable polymer" are frequently used interchangeably in the literature, the two categories of polymers [7] that deteriorate and eventually dissolve totally when subjected to microorganisms, aerobic, and anaerobic processes [8] have significant differences. The phrase "biobased" refers to polymers made from renewable resources. Renewable raw materials are those that are renewed by natural processes at rates that are equal to or faster than their rate of use. Two factors can be taken into account when classifying "biopolymers":

- The raw material's source;
- The polymer's biodegradability.

The compounds can be categorised as biopolymers when the two criteria for the division of polymer compounds, i.e., the source of origin of raw materials and their biodegradability, are taken into account. When the monomeric unit is made up of polysaccharides, glycosidic linkage is used to connect the linear or branched carbohydrate chains. These monomeric units include things like starch and cellulose. The amino acids that make up protein units are represented by collagen or fibrin, which are joined together by peptide bonds (amide linkage). Nucleic acids, which may be ordered in many ways in lengthy polymer chains made up of at least 13 units, make up the third category, which is a protein monomeric unit. DNA and RNA are two examples [9]. Both biological entities, such as plants and animals, as well as chemical synthesis from naturally occurring building blocks, such as maize, starch, etc., can form biopolymers. Dziuba et al. [10] addressed a thorough taxonomy of the biopolymers.

Biopolymers

Regarding the creation of composites with sensors utilised in many sectors of the economy and industry, biopolymers are crucial components. As sensitive components for building sensors employing biopolymers for chemical sensing in complicated settings, the flawless performances of biopolymers from biological chemical sensing systems make them ideal choices. Chemical sensing sensors utilising biopolymers and biomaterials have advanced significantly, presented useful views, and demonstrated prospective applications. The choice of a suitable polymer matrix is a crucial consideration when creating composite materials. Biodegradable polymers are increasingly being employed as matrices. The comparatively simple biodegradation of such materials is one of the key benefits of biodegradable polymers that contributes to their rising popularity. It is possible to regulate the material's biodegradation period by using a variety of additives, such as starch or montmorillonite [11]. Materials called composites have two or more chemically and physically distinct phases that are separated by a different interface. They are a combination of materials with various compositions, yet each individual component retains its individual personality. In short, composite materials are made of two or more components, one of which is found in the matrix phase and the other of which may take the shape of fibres or particles. Figure 1 demonstrates polymer composites with various reinforcements and matrix materials and illustrates the many forms of composite materials based on the polymer matrix.

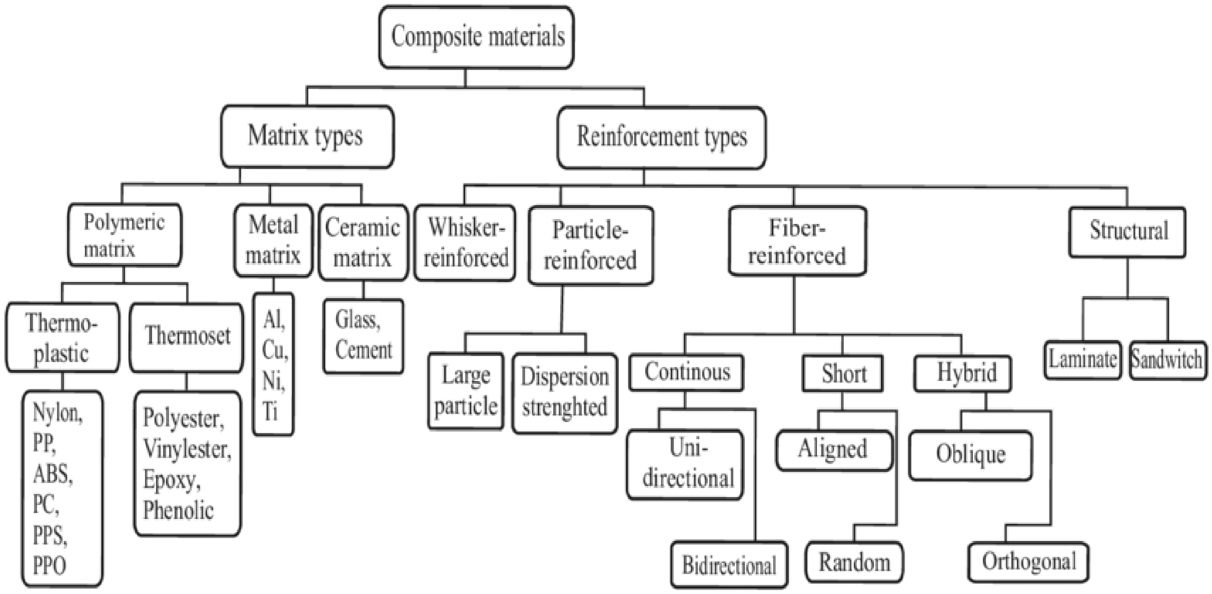

Figure 1: demonstrates the many composite materials based on the polymer matrix.

High thermal shock and creep resistance are characteristics of CMCs. With a longer tool life than cemented carbides, CMCs are made using hot pressing, hot isotactic pressing, and liquid phase sintering processes. They are utilised as cutting tool inserts for machining hard metal alloys. Ceramic composites increase a material's resistance to fracture [12–13]. A matrix material's filaments are meant to be carried by PMCs [14, 15]. Superior quality, mechanical strength, thermal stability, hardness, and stiffness are produced by modern fibre and grid composites [16, 17]. Glass fiber-reinforced polymers have fibres in a polymer network that range in diameter from 3 to 20 mm [18]. At lower temperatures, carbon fibres have the best quality and modulus [19], whereas at room temperature, carbon fibres are unaffected by moisture, bases, or acids [20]. Together, these many components work to provide the composite part the necessary mechanical strength [21]. Biocomposites are a unique class of polymer composites. When at least one component of a polymer composite is biobased or biodegradable, the composite is referred to as a biocomposit [22]. Biocomposites are made up of natural reinforcements (like vegetable fibres) and can either be fully biodegradable with biodegradable polymer matrices like renewable biopolymer matrices or partially biodegradable with nonbiodegradable polymer matrices like thermoplastic polymers (like polyethylene). The capacity to create a variety of qualities that may differ depending on the intended application of the composite is a benefit of composite materials. The primary benefit of these materials is their programmability, which currently enables widespread application in a variety of spheres of life, including building, industry, medicine, the manufacture of common items, and even spacecraft. Biocomposites and biopolymers with adjustable lifetimes are now hot subjects in a variety of application areas. The utilisation of biocomposites and sensors in conjunction with environmental and medicinal applications is the main topic of this article.

Biosensors

What a biosensor is is a crucial question that needs an answer. The physical identity may be obtained using this technique, which is subsequently converted into a distinguishable signal. To react as intended, it must be able to interact with various biological elements. The biosensor is capable of detecting biomolecules like urea, oestrogen, glucose, or cholesterol, for instance [23]. The biosensor is characterised by eight key factors:

1. Sensitivity, such as the concentration of the influencing factor;
2. Selectivity, such that only the predicted molecules will cause the sensor to react;
3. The range strictly relates to sensitivity and reflects the concentration range in which the sensitivity is active;
4. answer time, or how long it takes a biosensor to display 63% of the ultimate answer;
5. Reproducibility, the sensor's output's precision;
6. Detection, which caps the sensor's lowest detectable concentration;
7. 7.Lifetime is the period when the biosensor can be used without significant loss in performance;
8. Stability, whether there is any change in the baseline or sensitivity within a given period [24]. Lifetime is the amount of time that the biosensor may be operated without suffering a substantial performance loss. The manner of physiochemical transmission or the kind of bio recognition element (Figure 2) can both be used to categorise biosensors [25–27].

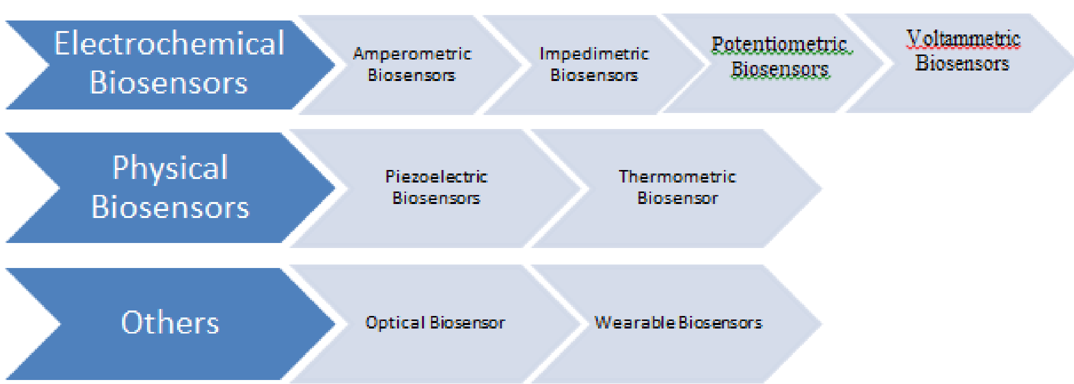

Figure 2: Classification of bio-sensors

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The manner of physiochemical transduction or the kind of biorecognition element can both be used to categorise biosensors (Figure 2). Due to their characteristics, electrochemical biosensors are the most extensively studied and described. They may be identified by their low detection limit, straightforward design, specificity, and simplicity of use [28]. Optical biosensors work when a biological process takes place that is linked to the absorption or emission of light. Associated techniques with this class of sensors include absorption, luminescence, fluorescence, surface plasma resonance, etc. Colorimetric sensors are the most researched because to the apparent colour change [29].

It makes sense to exploit the phenomena in the construction of biosensors since the majority of biological processes include a change in enthalpy and heat changes [30]. Utilising piezoelectric crystals, piezoelectric biosensors assess changes in mass by comparing them to variations in oscillation frequency. Biomolecular contact is the cause of this phenomena [30]. Conducting polymers (CPs), a unique family of biosensors, include massive resonation structures with many sp2 carbon atoms that allow for the delocalized movement of charge carriers. Among the group are synthetic metals like polyaniline (PANI), polypyrrole (PPy), polythiophene, and its derivatives [31]. The transducers that are used can also be used to classify biosensors. In this case, we can differentiate three generations. The first is made up of biosensors, which cause electrical reactions when reaction products diffuse to the transducers. The primary drawbacks of this group are a high applied potential and fluctuating product concentrations, which can cause interferences, a drop in electrical currents, and detection limits. The use of mediators between the reaction products and transducers was directly connected to the separation of the second generation. The mediator's lack of selectivity leads to a number of interfering interactions. The electrochemistry and biochemistry that take place as a semiconductor are the focus of the third generation of biosensors. High selectivity and sensitivity define this group [32, 33].

Composites made of carbon-based biopolymers provide unique advantages for biosensing. High surface area, conductivity, effective electron transport, and other characteristics characterize them. Biopolymer-MWCNT (multiwalled carbon nanotubes), which are deposited enzymes organophosphorus hydrolase-MWCNT and anionic DNA-MWCNT, is an example of employing carbon in biosensors and permits sensitive detection of paraoxon. When employed with a negatively charged polymer and graphene with enzymes embedded in biopolymers (like chitosan), a film may develop on the electrode, enabling the reagentless detection of H_2O_2 [33].

Correlation between Biopolymers and Biosensors:

The maintenance of the biological moiety's activity is closely connected to the proper operation of a biosensor. The choice of a matrix that guarantees sensor immobilisation and biocompatibility is crucial. Biopolymers are a fantastic choice for this because of their qualities. A large variety of biopolymers may expand in an aqueous environment, which aids in removing the analyte's diffusion barrier. Biopolymer-based composites are also extremely simple to make and have improved characteristics [23]. In order to generate the intended signal, it interacts with the target analyte. The sensor can be connected to the matrix using a variety of techniques. One of them employs physical adsorption, covalent binding, physical entrapment, and cross-linking to immobilise objects [23]. Numerous analytical methods have been employed to identify the presence of different contaminants. However, often, the need to carry the sample to the lab for examination is connected with their usage. Therefore, the creation of quick, portable environmental monitoring technologies is necessary. As an additional or alternative approach for analyte detection, biosensors appear to be a perfect answer. The International Union of Pure and Applied Chemistry (IUPAC) defines a biosensor as a self-contained integrated device with a biological recognition element (biochemical receptor) that is retained in direct spatial contact with a transduction element and is able to provide specific quantitative or semi-quantitative analytical information [33].

Biosensors for Environmental and Medical Applications

Environmental Application

One of the top goals of modern civilization should be protecting the environment and ensuring its security. The state of it directly impacts human health. However, the quantity of potentially dangerous contaminants shows that there is still a significant issue that has to be addressed. The safety of people, animals, and plants depends on the identification and monitoring of contaminants in every aspect of the environment [33]. In agriculture and the environment, biosensors are primarily used to monitor and detect the presence of pollutants and infectious diseases. Pesticides used on agricultural goods, radiation, and contaminants in the air and water may all be detected with biosensors. Biosensors can be used in the food industry to evaluate product quality, sustainability, and food safety [34]. According to the literature, the creation of biosensors inspired by nanotechnology has significantly advanced our understanding of chemicals whose dynamics have a striking impact on plant physiology [35]. Abiotic stress, plant diseases, phytohormones, metabolic content, and miRNA have all been detected by a variety of biosensors that have been developed [36].

Environmental Pollution

Applications for biosensors include the detection of environmental pollutants. Industry, agriculture, and other human-related activities are the principal sources of pollutants (both organic and inorganic) found in the environment [37]. Pesticides, potentially harmful substances, poisons, pathogens, and endocrine-disrupting chemical compounds are all monitored by biosensors in water, air, and soil [38]. Quantifying persistent toxicants is the focus of scientific study. Reusability and temperature and pH resistance are the key characteristics of biosensors employed as biodetection tools. Biorecognition is facilitated by a variety of biological components, such as enzymes, microorganisms, functional nucleic acids, antigens, antibodies, animal and plant tissue, and biomimetic materials (such as molecularly imprinted polymers) [39].

The frequent usage of some chemicals causes people to consider their impact on the environment. Tetrabromobisphenol A (TBBPA) and its derivatives, which are often employed as brominated flame retardants (BFRs), are among these chemicals. Due to its high toxicity and potential neurotoxins, the derivative tetrabromobisphenol A bis (2-hydroxyethyl) ether (TBBPA-DHEE) has caused considerable worry [40]. With the use of analytical instrumentation and immunoassay, it may be determined. The use of ultrasensitive competitive impedimetric immunosensors to concurrently detect TBBPA-DHEE and TBBPA-MHEE was described by Zhang et al. [41]. The analyte, coating antigen (coated on glassy carbon electrode (GCE)/chitosan (CS)/MWCNTsGONRs/gold nanoparticles (AuNPs), modified electrodes), and primary antibody (Ab1) were the foundation of the proposed system. The aquatic system may be monitored with the biosensor. Due to the water cycle and its significance in our everyday lives, monitoring water pollution is extremely important. The researchers [42] presented a simple biosensor made of non-disposable photodetector and disposable bioreporter pads (calcium alginate matrix containing immobilised bacteria). The authors investigated how the density of the bacteria, alginate concentration, and viscosity affected the sensor response. Its reactivity was tested in various spiking concentrations of many common and environmental contaminants, such as heavy metals, ammonium hydroxide, and formaldehyde. Small sample sizes, excellent sensitivity, and low detection limits were the hallmarks of the optimised product.

Pesticides

Herbicides and other pesticides pose a serious risk to the health of the environment and the ecosystem as a whole. The list of herbicides is extensive, and specific focus should be given to substances that hinder photosynthesis such urea, triazines, and phenolics. They frequently affect environments that are outside their intended targets, such nearby vegetation and freshwater ecosystems [43–44]. Herbicides can cause endocrine disruption, according to the literature [44], especially in situations of prolonged exposure. Biosensors are a fantastic replacement for time- and money-consuming classic analytical techniques including HPLC, AAS, and GC-MS. A new amperometric biosensor developed by the researchers [45] is based on direct suppression of the photocurrent produced by an artificial biofilm of photosynthetic bacteria. Living cells that were enclosed in an alginate matrix and bonded to the carbon-felt electrode were used in the creation of the sensor. Anabaena variabilis bacteria were immobilised in alginate capsules, resulting in a high cell density that is essential for bacterial stability. One of the frequent contaminants of soil and groundwater that is difficult for microorganisms to break down is trichloroethylene (TCE). The literature [46] describes the creation of a microbial biosensor based on the strain of Pseudomonas sp. that can identify the substance. To immobilise the microorganisms, a porous cellulose nitrate barrier was used. The transducer used was a chloride ion electrode [47]. The study examined various TCE and bacterial concentrations, pH values, temperatures, and interferences. The recognition element for the biosensor, Thiobacillus thioparus, was immobilised on a bed of agarose and sodium alginate. The detecting signal was thought to be an oxygen decrease. The authors verified that the oxygen taken up by the immobilised cells in the final biosensor was at a suitable level.

Wastewater

Another crucial task is wastewater monitoring. Heavy metal ion detection using the whole-cell electrochemical biosensor (Cu^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}) was published [128]. The Saccharomyces cerevisiae cells and the mediators were immobilised using an electrodeposited chitosan hydrogel polymer sheet that contained boron-doped nanocrystalline diamond particles. According to the research, it is possible to measure the acute toxicity of actual wastewater samples using the created indicator, which has promise for the online detection system. Electrochemical biosensors containing dye mediators can also be used for wastewater monitoring. A solution based on the use of an organic dye mediator (thionine) that employs electrostatic interactions to wrap E. coli was proposed by Fang et al. [48]. These microorganisms are the most prevalent Gram-negative bacteria that are frequently employed to evaluate the toxicity of substances. E. coli was changed on a glass carbon electrode after being immobilised in chitosan-entrapped carbon nanodot film. The usage of this electrode improved electron transport and boosted conductivity. A whole-cell electrochemical biosensor mediated by p-benzoquinone was created as another biosensor utilised in the evaluation of heavy metals (Cu^{2+}, Cd^{2+}), phenol (3,5-dichlorophenol), and insecticides. The coimmobilization of mixed strains of microorganisms (E. coli, B. subtilis, and S. cerevisiae) served as the foundation for the activity. Sodium alginate solution was used to create the microbial biofilm. The results of the investigation showed that the sensor may be utilised to estimate ecological risk with success [49].

Air Toxicity

Air is another element whose quality has to be monitored. To create a biosensor that allows for the monitoring of air toxicity, calcium alginate pads containing immobilised bacteria (E. coli) were utilised. The researchers [50] used paint, gasoline, weed killer, Tipex, bleach, oil strain remover, chloroform, and acetone as toxicants. All of these substances were present, simulating cellular reaction. The sensor showed that it could detect the presence of chemicals in an actual indoor setting. Synthetic polymers, which despise biopolymers, are frequently utilised in environmental control. The literature discusses their use in the detection of heavy metals in soil [52] and pesticides [51].

Measurement of Sweat Using Wearable Sensors

Sweat pH changes can be linked to a variety of clinical and physiological disorders. Sensitive components are often held captive in a hydrogel-like polymeric network. A change in the balance of electrostatic forces, such as reversible swelling or shrinking, might cause the responsiveness to become active. This is also susceptible to pH variations brought on by various illnesses. By co-polymerizing a 10 kDa poly(ethylene glycol)-diacrylate (PEG-DA) macromer with 2-carboxyethyl acrylate (CEA), a soft copolymer that, more critically, is pH sensitive may be created. The pH sensitivity of CEA as well as the attraction or repulsion of chains are caused by the carboxylic group, which is protonated in acidic conditions and deprotonated in basic settings.

Epidermal Injuries

The pH of the skin is somewhat acidic in healthy skin and ranges from alkaline to neutral in a wound between 7.15 and 8.93. Alginate-based microfibers loaded with pH-responsive silica beads that alter colour depending on the pH dye were the subject of Tamayol's investigations. Since hydrogel keeps the surrounding wet, its presence in healing wounds is advantageous. The healing process can be observed by changes in dressing colour. It was shown that improving wound healing is a possibility in addition to monitoring. Bovine serum albumin (BSA), a growth factor, was placed into a radical copolymerized hydrogel formed of poly(N-isopropyl acrylamide-co-acrylic acid) that continuously released at higher pH levels. Such a hydrogel may as well be filled with antibiotics, and when paired with the dye-based bacterial infection monitoring method, it produces a very efficient technique to improve wound care. Hyaluronic acid-infused hydroxyethyl cellulose hydrogel was created by Kwon et al. to treat skin lesions. The primary medication was slowly released because to the swelling and shrinking qualities caused by pH variations. At pH 7, the efficacy of such drug release was calculated to be greater than 70%.

Drug Delivery

Peptide drug delivery, which is ineffective in acidic environments, has also been studied using pH-sensitive hydrogels. Therefore, hydrogel protection offers a potential for effective medication delivery without loss. Yadav and Shivakumar achieved this goal by administering the medication to the intestines via soluble water chitosan. It was discovered that the concentration of the crosslinking agent, which was carboxymethyl chitosan and carbopol, had a significant impact on the hydrogel's sensitivity. This technique was used to treat nocturnal asthma by slowly delivering theophylline into the colon. In order to give the anticancer medicine as the pH adjacent to the tumour falls below the physiological range, a similar method of therapy was created by Dai et al. The ability of NIR light to quicken medication release was also demonstrated. Two polymers, DF-PEG-PAHy/BPNSs and N-(2-hydroxypropyl) methacrylamide (HPMA), were taken into consideration for this function. A pH-sensitive hydrogel and near-infrared (NIR) light were produced by mixing polyethylene glycol dimethacrylate (PEGDMA) and methacrylic acid (MAA) in a 1:2 molar feed ratio with ammonium sulphate. These materials also demonstrated perfect mechanical and swelling characteristics. The substance was evaluated in vivo as a drug delivery system for chemotherapy treatment using the chemical doxorubicin (DOX). The hydrogel structure effectively held the medication for cancer therapy, and it was then released in response to pH or NIR changes. The air-dried hydrogel is a composite made of graphene oxide and para-aminosalicylic acid following lyophilization. In both neutral and acidic environments, this mixture of polymers showed pH-sensitive characteristics as well as various drug release patterns. It is sensitive to changes in the internal pH of infected macrophages as well as changes in blood pH [53].

Perspectives

It appears that the development of biopolymer composites with sensors that can detect changes in the biological environment is still a ways off. What generates a region of immense potential is permeated and complemented by scientific disciplines. A solution to present and upcoming environmental and social issues, such as freshwater and ocean pollution, illnesses of civilization, an ageing population, and hereditary disorders, is made possible by the network of disciplines. The aforementioned issues serve as motivation for producers of indicator biocomposites in the fields of research, business, non-governmental organisations, and perhaps even government. Different drug release patterns in neutral and acidic settings and pH-sensitive characteristics. It is sensitive to changes in the internal pH of infected macrophages as well as changes in blood pH [54].

Summary and Conclusion

When creating biocomposites with sensors for use in a variety of applications, such as the environment or medicine, biopolymers are crucial. Biopolymer materials have a wide range of qualities that make them suitable for a wide range of industrial applications, including biosensors used in medicine. Biosensors are quick, mobile devices that make it possible to monitor their surroundings. These items are crucial for patient monitoring and medical diagnosis. Due to the usage of biological chemicals, tissues, and organisms, biosensors are well adapted to a range of diagnostic and real-time detection concerns. Health indicators may be monitored with medical biosensors. These medical resources support the development of point-of-care devices for illness diagnosis and prognostics by biomedical engineers, scientists, molecular biologists, oncologists, and clinicians. It also offers details on creating modality that can be transferred from the lab to the clinic that is user-friendly, sensitive, stable, accurate, inexpensive, and minimally invasive. A ageing population and the illnesses of civilization, such as diabetes, strokes, and disorders of the cardiovascular system, need the employment of novel medical treatments. Composites made of biopolymers and equipped with sensors that provide information on chemical and physiological factors are one future trend. These treatments will make it possible to treat difficult-to-heal wounds more quickly and efficiently, including pressure ulcers, diabetic foot ulcers, and wounds after major operations. They are required to increase patients' survival and functionality. Numerous research have been done by scientists, and medical advancements have far beyond even the most optimistic predictions of science fiction writers. With the science we have today, we can create highly sophisticated sensory technology. The cost of such materials, which make them pricey and challenging to get, is the only obstacle. However, their future development is guaranteed, and the costs will come down. Human health and life are difficult to quantify, hence modern technology should be used in medical treatment.

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