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Review

A Review of Investigations and Applications of Biocides in Nanomaterials and Nanotechnologies

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Abstract: In recent years, the development of nanomaterials with biocidal properties has received considerable attention due to their potential applications in various industries, including food, medicine, and cultural heritage preservation. The growing demand for coatings with antibacterial properties has sparked interest from industrial sectors in exploring the incorporation of biocides into these materials. Coatings are prone to microbial growth, which can cause damage such as cracking, discoloration, and staining. To combat these problems, the integration of biocides into coatings is a crucial strategy. Biocide-embedded nanomaterials offer numerous advantages, including high efficiency in small quantities, ease of application, good chemical stability, low toxicity, and non-bioaccumulation. Encapsulated nanobiocides are particularly attractive to the agro-industry, because they can be less toxic than traditional biocides while still effectively controlling microbial contamination. To fully exploit the benefits of nanobiocides, future research should focus on optimizing their synthesis, formulation, and delivery methods. The purpose of this review is to summarize the current status of biocide nanomaterials, discuss potential future research directions, and highlight research methods, the development of new forms of nanomaterials, and studies of their physico-chemical properties. Biocide nanocapsules of DCOIT (4,5-Dichloro-2-octyl-2H-isothiazol-3-one) are chosen as an example to illustrate the research pathways.

Keywords: nanomaterials; biocide; microencapsulation; nanoparticles; microcapsule

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1. Introduction

Biocidal nanomaterials refer to a class of nanoscale materials that exhibit antimicrobial properties. These materials have gained significant attention in recent years due to their potential applications in various fields, such as healthcare, food packaging, water treatment, and consumer products.

The unique properties of nanomaterials arise from their extremely small size, typically ranging from 1 to 100 nanometers. At this scale, materials can exhibit different chemical, physical, and biological properties compared to their bulk counterparts. Biocidal nanomaterials take advantage of these properties to effectively control microbial growth and eliminate harmful pathogens [1].

A huge number of bacteria, fungi (molds, yeasts, etc.) living in water, soil, and living host organisms are suspended in the air. Accumulating on various surface areas [2], microbes begin to proliferate intensively, even with minimal opportunities, rapidly forming a surface film (or biofilm) consisting of colonies of various microorganisms, distributed in a continuous matrix of extracellular polymeric substances [3]. Periodically, microcolonies detach from this film, contributing to the further spread of microbial contamination/infection by attaching to new surfaces. This mechanism can have particularly adverse effects in cases of proliferation and dissemination of dangerous pathogenic microbes with toxic metabolic products, such as mycotoxins, on coatings that are intended for indoor use. Hence, various antimicrobial coatings are employed for prevention and protection against such occurrences [3,4], the specific nature of which is determined by the type of microorganisms to be eliminated (bacteria, microscopic fungi, etc.) Additionally, the formation of microbial films represents the initial stage of a phenomenon known as biofouling [5,6], which particularly affects shipping, as well as marine and port infrastructure. Serving as a nutrient medium for various aquatic organisms/animals, biofilm with microorganism colonies facilitates the attachment of such parasite organisms to the surfaces of numerous objects related to maritime and river transport spheres and their corresponding infrastructure (marine and river vessels, docks, offshore oil platforms, wind energy installations, etc.).

Biocidal products are used to preserve goods, control pests like insects or rodents, and control viruses, bacteria, and fungi through a chemical or biological action. Common examples are disinfectants, wood preservatives, and insect repellents [7]. Typically, biocidal nanomaterials are composite materials which include the "active substance" that has a controlling impact on the endangered organisms.

One of the key advantages of biocidal nanomaterials is their ability to exhibit enhanced antimicrobial efficacy compared to traditional antimicrobial agents. Nanoscale materials have unique physical, chemical, and biological properties that enable them to interact more effectively with microorganisms. These properties include a high surface-area-to-volume ratio, increased reactivity, and the ability to penetrate biological membranes [7].

Understanding the correlation between the chemical structure of biocides and their antimicrobial activity is essential for the development of effective and safe antimicrobial agents.

To the best of our knowledge, there is a lack of reviews which cover the different types of biocides by nature, application, production methods, and their physico-chemical and antimicrobial properties. This review presents a summary and discussion of the current state of art of nanomaterials with biocides, including potential future directions for research, methods for their investigation, and the development of new forms of nanomaterials. This review explores the relationship between biocide structure and activity, encompassing different classes of biocides and various factors influencing the antimicrobial efficacy of biocides.

2. Types of Biocides by Application

Due to their properties, biocidal nanomaterials can be used in almost any industry, since they perform the main antimicrobial and protective functions shown in Figure 1.

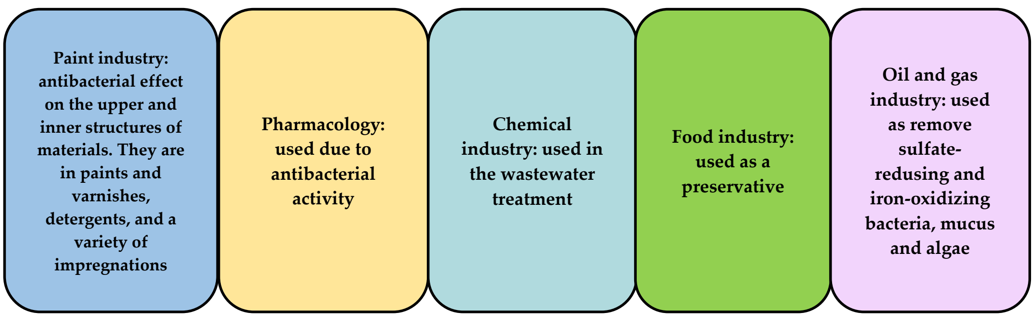


Figure 1. Types of applications of biocides in various industries.

There are different types of biocides depending on their use, which are shown in Table 1.

Table 1. Types of biocides according to their use.

Types of Biocides	Application	References
Insecticides	Used to kill insects. It is more commonly used in the production of textiles and wood products.	[8]
Acaricides	Act as tick repellents.	[9]
Herbicides	Used for vegetation (weeds) destruction. They are used in areas where vegetation can cause problems, such as roadsides and airfields.	[10]
Bactericides	Used to kill bacteria and in water treatment, for the stabilization of drilling fluids, protection against corrosion, and biodegradation.	[11]
Antibiotics	Drugs that are used to treat bacteria, not only in medicine, but also in the food and agriculture industries.	[12]
Fungicides	Used to kill fungi and mold, are applied in agriculture, floriculture, and greenhouses.	[13]
Zoocides	Used to kill harmful small rodents and birds.	[14]

Different types of nanomaterials with biocides have been developed and studied extensively. Some nanoparticles, such as silver, copper, titanium oxide, and zinc oxide nanoparticles, can be incorporated into various matrices such as coatings, textiles, and polymers to provide long-lasting antimicrobial effects [15].

Despite the fact that biocidal nanomaterials have significant potential, it is essential to consider their potential impacts on human health and the environment. The release of nanoparticles into the environment or their prolonged exposure to humans could raise some concerns. Extensive research is being conducted to address these issues and ensure the safe use of biocidal nanomaterials [16].

Biocidal nanomaterials can be considered a promising approach to control microbial contaminations in various applications. Their unique properties and enhanced antimicrobial efficacies make them attractive alternatives to traditional antimicrobial agents. However, further research is needed to fully understand their potential risks and implement appropriate safety measures [16].

3. Types of Biocides by Nature

In terms of nature, biocides can be divided into organic and inorganic. Inorganic biocides are effective and inexpensive, and they are widely used for water disinfection in drinking ponds and swimming pools. They are used in hospitals to disinfect surfaces, in the food industry during packaging in foil containers for disinfection, to bleach materials, as well as to kill bacteria. Bacteria are killed with ozone rather than chlorine in many municipal drinking water systems. Over the last 50 years, a wide range of biocides have been used to preserve materials. Mercury-based biocides, which were previously used, had the potential to meet the needs for canning and dry storage of paints or coatings from all types of microorganisms. Tin biocides are widely utilized as antifouling agents in marine paints. However, due to their toxicity and environmental concerns, these agents are being phased out [17,18]. Table 2 summarizes some inorganic biocides and their characterization.

Organic biocides are chemical compounds that contain carbon and are commonly used due to their effectiveness in controlling biological growth. Depending on the types of organic biocides, the mechanism of action, target microbes, and routes of application also differ. It is important to use organic biocides that are safe to humans, animals, and the environment [37]. Table 3 shows the types of some of the most commonly studied organic biocides that are used in various industries.

Table 2. Some inorganic biocides and their characterization.

Inorganic Biocides	Combination with Components	Used Concentration	Solubility	Application	References
Boric acids, Borates	1. Pyroligneous acid (48.2% and 54.6%); 2. Tall oil (90%); 3. PVP-Se NPs in mixture of commercial fungicide containing boric acid, alkylbenzyldimethylammonium chloride, and ethanolamine.	1%, 2%, 8%	water, methanol	Fungicide	[19–23]
Sodium Dichromate	Nanoporous Cr-Mn-Fe oxide	15–30%	water	Fungicide	[24,25]
Ammonium Silicofluoride	Sodium silicate solute	20%	water	Fungicide, 5% solution	[26,27]
Sodium metasilicate	Chitosan (51–99%)	0.18–2%	water	Fungicide	[28–30]
Copper sulfate	CuCaps obtained by microcapsulating a mixture of copper sulfate–copper hydroxide	Copper sulfate (18.84%) and copper hydroxide (3.84%)	water	Bactericide	[31,32]
Sodium fluoride	Colloidal chitosan–silver nanoparticle–fluoride nanocomposites	1.025 g/L	water, methanol, ethanol	Fungicide	[33,34]
Chlorine	UV (99%)	1 mg/L	water	Fungicide	[35,36]

Table 3. Some organic biocides.

Organic Biocides	Characterization	Used Concentration	Solubility	Application	References
Dithiocarbamates	$ZnCl_2$ $CuCl_2$	10 µg/mL	water, polar organic solvents	Fungicide	[38,39]
2-Mercaptobenzothiazole	Silica nanoparticles	20–200 mg/L	water, organic solvents	Biocide	[40,41]
4-hydroxybenzoate	Diphenyltin (IV) oxide	5×10^{-4} M	weakly in water, well in alcohols, esters, and ketones	Fungicide	[42,43]
2,4,4′-trichloro-2′-hydroxy-diphenyl ether	Calcein	10 µg/L	water	Fungicide	[44,45]
2,2-Dibromo-3-Nitrilopropionamide	Silver nanoparticles	from 45 to 1.250 mg/L	polyethylene glycol, benzene, ethanol, and other organic solvents, weakly in water	Biocide	[46,47]
DCOIT	Silica nanoparticles	10 wt%	organic solvents, weakly in water	Fungicide, bactericide	[48]
Benzisothiazolinone	Mg-Al layered double-hydroxides (LDH)	5 wt%	alcohols, weakly in water	Fungicide, bactericide	[49,50]
Bromo nitropropane diol (Bronopol, Myacide AS)	Copper sulphate (inhibition zone 21.6 mm)	250 ppm	water, alcohols, acetic acid, diethyl ether, and ethyl acetate, weakly in chloroform, acetone	Bactericide	[51,52]
Cetylpyridinium chloride	SiO_2, TiO_2, calcium montmorillonite	16–128 µg/mL 13.44 mg/g–48.83 mg/g	water, ethanol	Disinfectant	[53–55]
N-3,4-dichIorophenyl-N, N-dimethylurea (Diuron)	Cyclodextrin	5–15 mg/L	ethanol, acetone	Herbicide	[56,57]
Glutaraldehyde	Chitosan with glycerol (0, 10, 20, and 30% *w*/*w*)	0.99 mg/150 mL	water, alcohol, ether, other organic solvents	Fungicide, bactericide	[58,59]
3-iodo-2-propynyl butylcarbamate	Dimethyl sulfoxide	0.74–2.21 mg/mL	organic solvents	Fungicide, bactericide	[60,61]
N-cetyl-N,N,N-trimethyl ammonium bromide	Zinc sulphate + oxalic acid. 99.48%	40 ppm + 25 ppm	Completely soluble acetone	Biocide	[62]

The biocides can be encapsulated or embedded in the matrix in their pure form [63–65]. Biocides can also be tethered to polymeric matrices to prevent biocide release into surrounding water [66–68].

4. Types of Nanoparticles Used for Microencapsulation

The use of biocides that are encapsulated by nanoparticles is a new use of nanomaterials that have shown great potential in various fields, such as in medicine, the food industry, and water treatment processes. These materials are composed of nanoparticles and biocidal agents that are enclosed in microcapsules, which provide numerous advantages in terms of protecting the bioactive substances, increased efficiency, and the possibility of a controlled release [69,70].

Nanoparticles can be produced chemically or biologically. Metallic nanoparticles have a wide range of applications in industries, including gold, silver, alloys, magnetic materials, and many others, typically made of natural or synthetic polymer materials [71]. They are stable, functional, and biologically active. Due to the encapsulation, nanoparticles can load functional molecules to improve their stability and performance. Peptides, for example, are commonly embedded in the inner layer of nanoparticles to improve nanoparticles' stability. Nanoparticle preparation methods primarily include ionic crosslinking, covalent crosslinking, and polyelectrolyte complexation [72].

Silver ions and salts have long been recognized for their antimicrobial properties; however, the effects of Ag nanoparticles on microorganisms and their antimicrobial mechanism remain unclear. Ag nanoparticles were tested for their ability to inhibit the growth of yeast, *Escherichia coli*, and *Staphylococcus aureus*. As a result, at low concentrations of Ag nanoparticles, growth-inhibitory effects on yeast and *E. coli* were inhibited, while mild effects were observed on *S. aureus*. According to the authors, silver nanoparticles have the potential to function as efficient growth inhibitors in a range of microorganisms, rendering them suitable for use in a variety of medical devices and antimicrobial control systems [73].

Silver nanoparticles or silver ions are primarily used in the formulation of paints. Silver ions act directly act in the metabolism of bacteria, inhibiting nutrient conversion and bacterial survival, reproduction, and colonization [74]. In [75], the authors present a review of the antibacterial effects of silver nanomaterials and propose antibacterial mechanisms and possible toxicity to higher organisms. Silver nanomaterials appear to exert bacteriocidal activity, predominantly through the release of silver ions, followed (individually or in combination) by increased membrane permeability and a loss of the proton motive force.

In the work [76], a novel synthetic scheme is presented for producing a nanoparticle–pesticide core–shell conjugate that can be used as an active agent against arthropod vectors such as mosquitos.

Gold nanoparticles possess the ability to impede bacterial growth by attaching themselves to the surface of bacterial cells through surface modifications. These alterations trigger the release of reactive oxygen species, which result in protein destabilization, DNA degradation, impairment of mitochondrial functions, and ultimately, lead to cell death. A research endeavor documented the production of gold nanoparticles using Mentha piperita and assessed their impact on *E. coli* and *S. aureus*, revealing that gold nanoparticles exhibited antibacterial properties solely against *E. coli*. [69].

Metal–oxide nanoparticles with antimicrobial properties (such as AgO, ZnO, TiO_2, SiO_2, and MgO) are reported in a variety of fields, such as textiles, packaging, cosmetics, and biomedicine.

Other metal oxides with photocatalytic activity, such as ZnO, TiO_2, SiO_2, and MgO, can release reactive oxygen products that kill bacteria when exposed to UV radiation. Zinc oxide and other zinc complexes, in particular, have been used as dry-film preservatives in exterior coatings to inhibit the growth of fungi and algae. The addition of ZnO nanoparticles to a water-based acrylic latex coating results in stable dispersions with improved physicochemical, mechanical, and anticorrosive properties, as well as antimicrobial resistance at a lower concentration than biocides in commercial paints [46].

Interior paints that are water-based acrylate dispersions with MgO nanoparticles, on the other hand, provide antimicrobial properties due to the morphology of the nanoparticles (sharp edges) and the formation of reactive oxygen species that induce lipid peroxidation in bacterial cells [46].

Functionalized SiO_2 primarily inhibited the growth of algae in dry paints and was also advantageous because of its non-leaching properties. However, future metal nanoparticle applications must be subjected to toxicity risk assessments.

Carbon nanotubes (CNTs) have shown potential as antimicrobial agents too. They can disrupt bacterial membranes and inhibit the growth of bacteria. CNTs are used in various applications such as wound dressings, filters, and coatings for their antimicrobial properties.

Chitosan nanoparticles derived from chitin, a natural polymer, possess excellent antimicrobial properties. They have been used in wound dressings, drug delivery systems, and food packaging materials to prevent microbial contaminations [77].

It is important to note that the choice of nanoparticles depends on the specific application and desired antimicrobial effects. The incorporation of nanoparticles in conjunction with encapsulation offers a crucial approach to enhancing the efficacy of biological agents in challenging environmental conditions. In [78], Bacillus velezensis was entrapped within alginate capsules, along with whey protein and gums like zedo, mastic, and tragacanth, in the presence of silica and titania nanoparticles. This resulted in the creation of innovative microencapsulation systems consisting of two-layer and multilayer structures. Notably, the multilayer formulation of alginate–whey-protein–zedo gum exhibited the highest encapsulation efficiency, reaching an impressive value of 94.3%. To ascertain the efficacy of the encapsulation process, X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy confirmed the successful integration of the alginate, whey protein, and zedo gum, without the formation of any chemically incompatible compounds.

In comparison to ordinary nanoparticles, biocompatible or so-called "green" nanoparticles provide a variety of advantages, because their production is environmentally friendly and does not involve the use of hazardous chemicals, high temperatures, or pressure [79].

5. Synthesis and Characterization of Microencapsulated Biocides with Nanoparticles

There are several steps to synthesize microencapsulated biocides using nanoparticles. As the first step, chemical precipitation, laser ablation, and emulsion polymerization can be used to synthesize the nanoparticles [80]. The second step is the incorporation of biocides into the nanoparticles by adsorption or encapsulation. The third step is the encapsulation of nanoparticles in polymeric shells to form microcapsules. In [81], sub-microcontainers of biocides were obtained using a Pickering emulsion. Figure 2 shows a schematic representation of the processes required for obtaining containers by using nanoparticles.

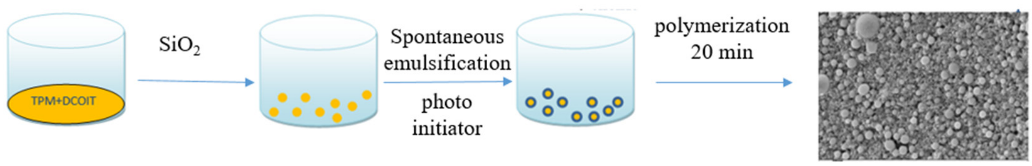


Figure 2. Schematic representation of the production of microcapsules by using nanoparticles [81].

The encapsulation of biocides is a widely used method to optimize their release rate and is employed across various industries, such as pharmacology, food, medicine, cosmetics, and agriculture. This approach offers several advantages, including protection against degradation and modification of their properties, controlled release rates, compatibility of typically incompatible compounds, and improved stability. In the field of anticorrosive coatings, where corrosion inhibitors are encapsulated in microcapsules and triggered for release by external stimuli like pH changes, this concept has been studied extensively.

In the context of biocides for antifouling coatings, there has been significant exploration of the use of oil-in-water emulsions and polymeric microcapsules for encapsulation purposes. Microcapsules are commonly used to protect UV-sensitive biocides such as 3-iodo-2-propynyl butylcarbamate and prevent the premature release of easily degradable biocides [82]. Additionally, microcapsules aid in coating formulations and prevent undesired plasticization of the coating films. However, it should be noted that the release from nonporous microcapsules typically involves the rupture and immediate release of the biocide, which can lead to a peak-like delivery pattern that may not be desired. Furthermore, it is important to incorporate free biocides in the coating besides microcapsules to effectively control microorganisms [82].

6. Properties of Microencapsulated Biocides with Nanoparticles

Microencapsulated biocides with nanoparticles possess several unique properties that make them highly effective in controlling microbial contaminations. These properties include the following factors:

1. Controlled release: Microencapsulation enables the controlled release of biocidal agents, ensuring that these agents are gradually available over long periods of time. Controlled release is utilized in various fields, but it was originally developed in the pharmaceutical industry [72]. It can be categorized as triggered, fast, or sustained release. One can try to achieve sustained release, where the biocide is steadily released from the microparticle over an extended duration. Ideally, the release would occur at a constant rate, known as zero-order release, which can theoretically be achieved by dispersing the active ingredients as crystals in the capsules' core [83].

There are various release mechanisms of encapsulated active substances [84]. In microparticle systems, the controlled sustained release of an active substance is determined by the permeation through the shell and the coating matrix.

The solubility of a biocide in the microcapsule shell, the core material, and the surrounding medium (such as a paint or an aqueous solution) will determine its distribution between the phases.

This is stated by the partition coefficient, $K^i_{A/B}$, of the active compound i between phases A and B:

$$K^i_{A/B} = \frac{c^i_A}{c^i_B} \quad (1)$$

where c^i_A and c^i_B are the equilibrium constants of active i in phases A and B, respectively. The partition coefficient $K^i_{A/B}$ is a thermodynamic constant.

In [81], the release rate of the biocide DCOIT from sub-micron containers was examined using spectrophotometry in a simulated water–ethanol mixture (1:1), ensuring that there were sufficiently high concentrations of the biocide to be detectable at the initial stage of the release process. It was observed that the maximum release of the encapsulated DCOIT occurred after approximately 24–27 h.

2. Protection: Polymeric shells offer excellent protection against external factors such as light, heat, and moisture, which can degrade bioactive substances. Microencapsulation is a highly effective technique for protecting sensitive components. By selecting the appropriate coating material for the encapsulation, controlled release ensures the complete delivery of the encapsulated components [85].

Biological biocides have the potential to reduce plants' biotic stresses and boost their development, but they tend to be unstable and degrade quickly. In [86], the authors investigated biological control agents which inhibit plant diseases and enhance crop productivity while being eco-friendly.

3. Enhanced efficiency: Microencapsulated biocides containing nanoparticles have demonstrated superior antimicrobial activity compared to other biocidal agents. Various parameters, as illustrated in Figure 3, can influence the encapsulation efficiency of microparticles, microcapsules, or microspheres.

Controlled release technology offers targeted benefits that vary across different applications. It enables the use of the most effective concentration of active target substances by preventing excessive release and destruction. By adjusting the internal factors of the carrier system, it becomes possible to achieve object-specific or targeted delivery of agents. The release process can be slowed down through the manipulation of various control parameters, allowing for a less frequent administration of the active agent.

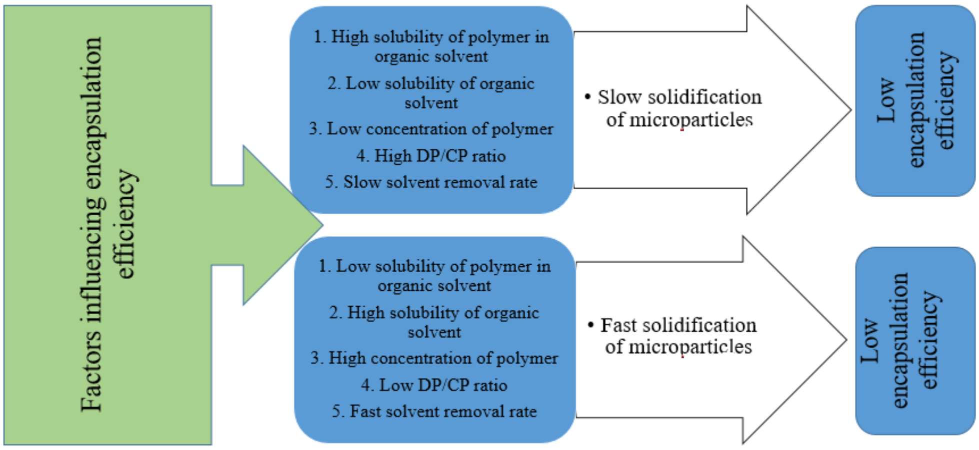


Figure 3. Factors influencing encapsulation efficiency.

In [87], the use of biodegradable polymers in the field of agriculture, specifically focusing on their production methods, degradation mechanisms, and release kinetics, is discussed. Once the substances are encapsulated and delivered, the next step is to release the contents from the media volume.

In [88], the potential release of protein from dextranase in various media is investigated. They demonstrated the correlation between the release rate of a Bauman–Birk-type protease inhibitor and the pH of the medium, as well as the presence of dextranase. The study revealed that within a day, at the optimum pH for dextranase activity, the protein was completely released, with an 82% activity level, indicating its resistance to inclusion and degradation processes.

The release rate of thyme oil through polylactide microcapsule walls was examined in [89]. The findings showed that thymol release was most rapid in the first hour and maintained a relatively constant rate in subsequent days. Additionally, polar compounds in thyme oil were released more quickly compared to non-polar compounds.

A novel type of microcapsules with a customizable active release mechanism was presented in [90]. These capsules were triggered by a plasticizing stimulus that induces a phase transition of the polymer membrane, transferring it from a solid to a fluidized state. Consequently, the cargo was actively displaced from the capsule through a controlled-release kinetic defect in the capsule wall.

4. Targeted delivery: Microcapsules can be specifically designed to release biocidal agents at precise target sites, ensuring targeted delivery and minimizing the loss of bioactive substances. Compared to traditional delivery systems, microencapsulated systems offer potential advantages. Consequently, both controlled release and targeted delivery can be achieved through the utilization of microcapsules and microspheres [91].

In a review, the authors provide a systematic overview of specific properties of nanostructured materials, such as inorganic nanoparticles, polymeric micelles, chitosan, liposomes, dendrimers, carbon nanotubes, quantum dots, and niosomes, and consolidate their therapeutic approaches in the diagnosis and treatment of chronic diseases such as cancer, COVID-19, and HIV/AIDS [92]. For effective drug delivery, factors such as nanomaterial interactions with the physiological environment, the mode of drug administration, the therapeutic agent's stability, and the mechanism of action have been summarized, and also, the advantages and disadvantages of nanomedicines in drug delivery have been discussed. Future advancement in the domain of nanotechnology-mediated advanced drug delivery systems is required by combining newer treatment approaches such as gene therapy and immunotherapy with existing nanotechnologies to improve drug performance and maximize the efficiency of targeted drug distribution [93,94].

7. Antimicrobial Activity of Biocides

The agro-industry is particularly vulnerable to contamination by microorganisms such as bacteria, fungi, and viruses, which can result in food spoilage, decreased yields, and health hazards. Nanobiocides offer a promising solution to these issues, as they exhibit high efficiency and improved targeting capabilities compared to traditional biocides. The encapsulation of biocides further enhances their stability, reduces toxicity, and prolongs their effectiveness [95,96].

DCOIT is a widely utilized biocide, and it demonstrates strong effectiveness against a wide range of microorganisms and is chosen as an example in this review to illustrate the research pathway and steps of the investigation. However, its limited water solubility and high toxicity hinder its application in the agro-industry. Nanoscale encapsulation of DCOIT presents an appealing solution to these challenges by mitigating its toxicity and enhancing its water solubility [79]. The encapsulation process not only enhances the stability of DCOIT but also prolongs its antimicrobial activity. Numerous studies have demonstrated the high antimicrobial efficacy of DCOIT encapsulated in different nanomaterials, such as polymeric nanoparticles, silica nanoparticles, and liposomes, specifically when applied in the agro-industry [81].

Micro- and nanocapsules with a polyurea shell and a DCOIT core produced by surface polycondensation on oil-in-water emulsion droplets (Figure 4a) [96], with a shell of silicon dioxide nanoparticles and a polymethacrylate core with DCOIT included in it using a Pickering emulsion followed by polymerization (Figure 4b) [81], were obtained. Figure 4 shows a scheme for the synthesis of microcapsules with biocide DCOIT.

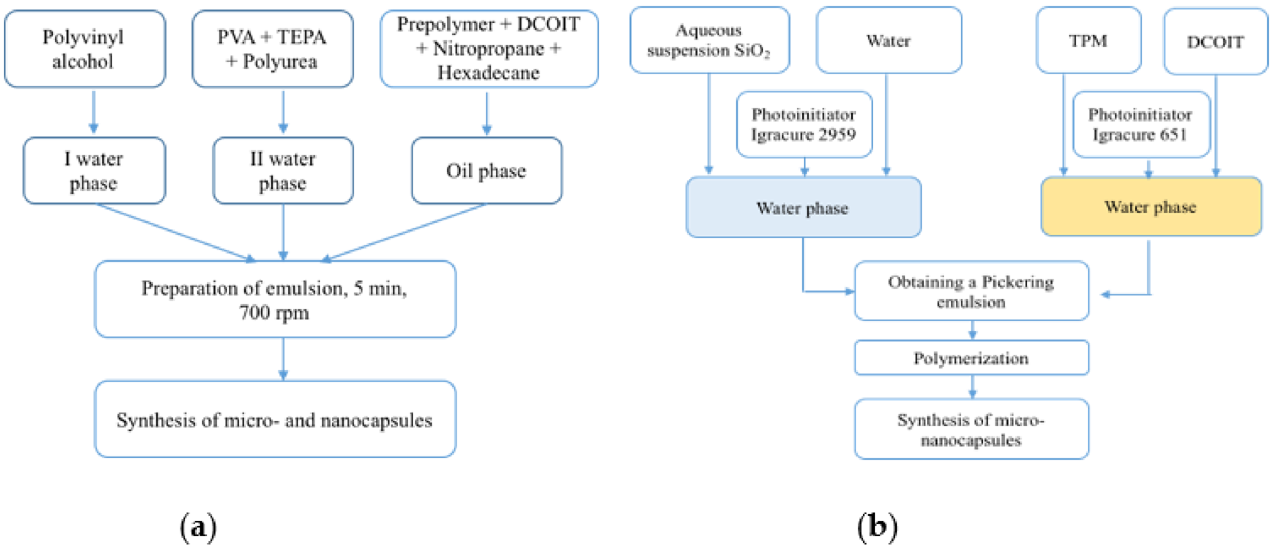
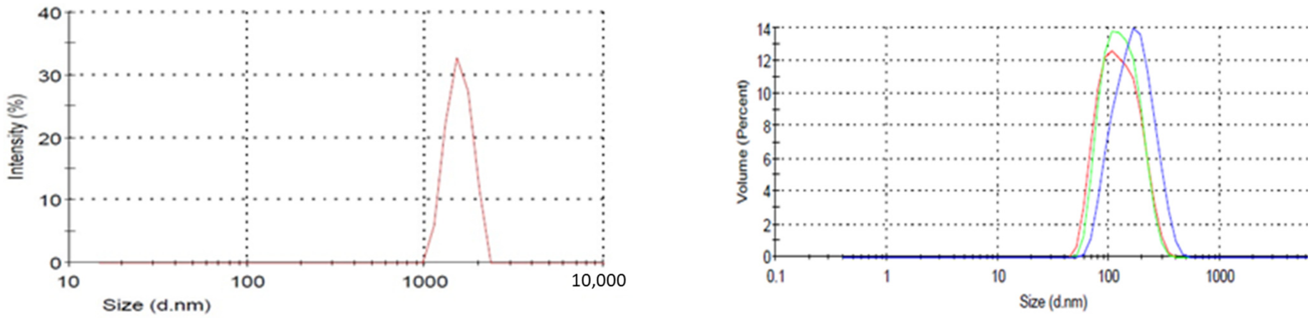


Figure 4. A scheme for the synthesis of microcapsules loaded with the biocide DCOIT (**a**) for microcapsules with a polyurea shell and DCOIT biocide in the core and (**b**) for microcapsules with a shell made of silicon dioxide nanoparticles and a core of polymethacrylate containing DCOIT.

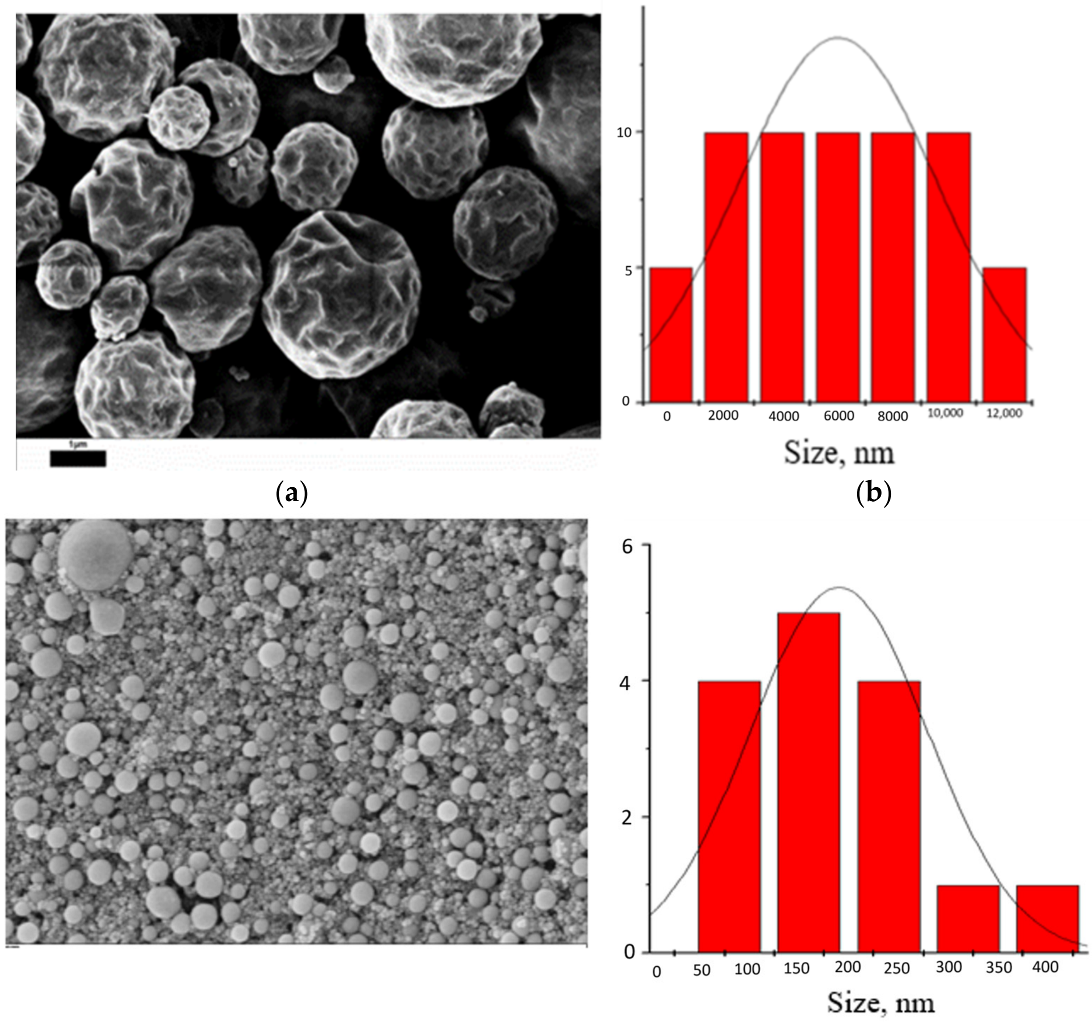
The physico-chemical properties of the obtained micro- and nanocapsules loaded with the biocide DCOIT and studied by DLS showed high monodispersity in the case of a shell made of silicon dioxide nanoparticles and a core of polymethacrylate with DCOIT. It is also worth noting that the Pickering emulsion droplets had the same low polydispersity prior to polymerization, with the exception that the particle size after polymerization was slightly larger than the initial droplet size (Figure 5).



(**a**) (**b**)

Figure 5. Particle size distribution of (**a**) microcapsules with a polyurea shell and DCOIT biocide load in the core [96] and (**b**) microcapsules with a shell made of silicon dioxide nanoparticles and a core of polymethacrylate containing DCOIT: red line—before filtration; green line—after polymerization, blue line—after polymerization [81].

The capsule particle sizes (Figure 5b) were confirmed by SEM micrographs (Figure 6), showing their spherical shape.



(**a**) (**b**)

(**c**) (**d**)

Figure 6. SEM micrographs and particle size distribution curves: (**a**,**b**) microcapsules with a shell made of silicon dioxide nanoparticles and a core of polymethacrylate containing DCOIT [40]; (**c**,**d**) microcapsules with a polyurea shell with DCOIT biocide in the core [96].

Studies of the release of DCOIT show that there is a slow kinetics of biocide release and even after several weeks, the concentration of the biocide that is necessary for effective action on microorganisms is not achieved. Based on the release kinetics, it was determined that DCOIT diffuses very slowly through the walls of the microcapsules with polyurea shells, making them unsuitable for use in nanostructured antimicrobial coatings.

The necessary concentration of the biocide for an effective action against most microorganisms was attained in a water–ethanol medium (Figure 7).

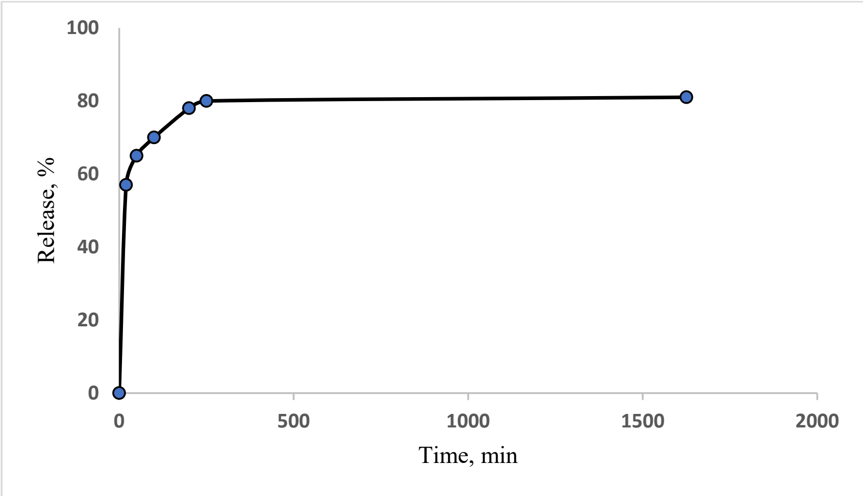


Figure 7. Biocide release rate from micro- and nanocapsules with a shell made of silicon dioxide nanoparticles and a core of polymethacrylate with DCOIT [81].

The positive effect of encapsulating the DCOIT biocide into micro- and nanocapsules, consisting of a prolonged inhibition of microbial growth of up to 70% after 15 days (Figure 8), was confirmed by statistically reliable tests of biological activity [81].

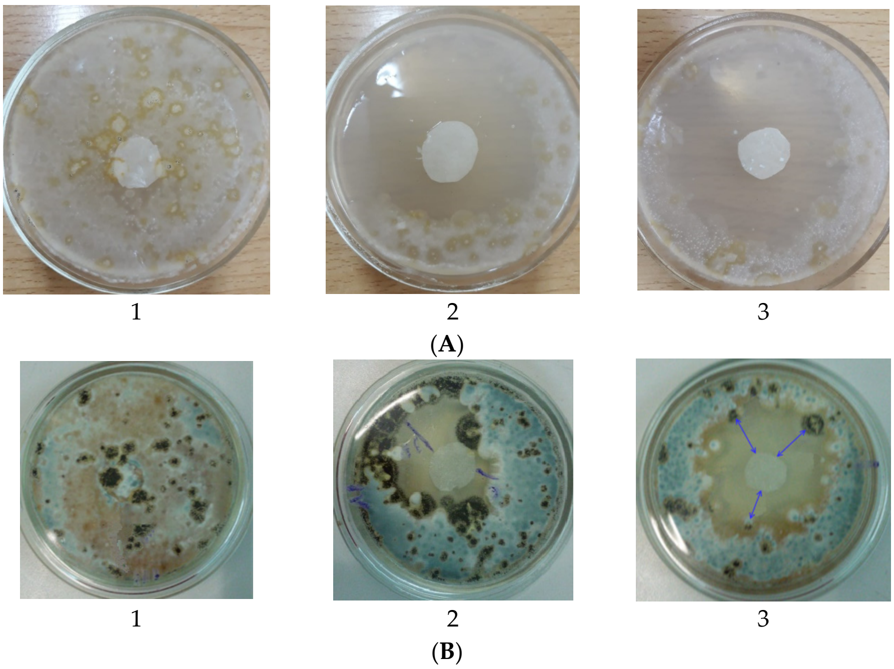


Figure 8. Comparison of the effectiveness of inhibiting the growth of Aspergillus niger after (**A**) 5 days in empty sub-microcontainers (1) (similar to control with free growth of microorganisms), biocide in free form (2), encapsulated biocide (3); (**B**) the same as A but after 15 days where blue arrows corresponds to inhibition zone (3) [81].

A positive effect of the addition of an antimicrobial biocide into micro- and nanocapsules with protective properties with a shell of SiO_2 nanoparticles and a core of polymethacrylate into protective coatings against mold fungi and bacteria, as well as against biofouling, was revealed in [81].

8. Future Research Directions

While the potential of nanosized encapsulated DCOIT in the agro-industry is promising, additional studies are necessary to enhance its formulation, delivery, and practical implementation. It is crucial for future research to concentrate on improving the biocompatibility and environmental implications of DCOIT, as well as enhancing its efficacy against specific pathogenic microorganisms. Furthermore, careful evaluation of the safety and regulation of nanosized encapsulated DCOIT in the agro-industry is relevant and necessary.

9. Conclusions

Biocidal nanomaterials offer a wide range of potential applications in various fields, such as wastewater treatment, food packaging, and biomedical devices. However, their effectiveness depends on their properties and the mechanisms by which they exert their antimicrobial effects.

Encapsulated nanobiocides have demonstrated promising antimicrobial properties against different microorganisms in the agro-industrial complex, highlighting their potential to control microbial growth and mitigate associated risks. These encapsulated nanobiocides are promising for an effective management of microbial growth in the agro-industry, while being potentially less toxic than traditional biocides. To maximize their benefits, future studies should focus on optimizing the synthesis, formulation, and delivery methods of these nanomaterials in the agro-industry.

The encapsulation of DCOIT into nanomaterials provides a potential solution to address the challenges related to low water solubility and high toxicity, making it a promising biocide for controlling microbial contaminations in the agro-industry. Extensive research has been conducted on the antimicrobial activity and delivery systems of nanosized encapsulated DCOIT. Further investigations should aim to optimize its efficacy, biocompatibility, and environmental impact to ensure its successful implementation in the field.

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