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Microorganisms and Carbon Nanotubes: Interaction and Applications (Review)

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Abstract—The review addresses various aspects of the interaction between carbon nanotubes (CNTs) and microorganisms: the antimicrobial effects of single-walled, multiwalled, functionalized, and nonfunctionalized CNTs; the mechanism of action of these nanomaterials at the single-cell level; and their effects on soil and aquatic microorganisms. Among the mechanisms of action of CNTs on the microbial cell, one should note direct contact, which leads to disruption of the cell wall and cytoplasmic membrane, changes in membrane fluidity, oxidative stress, enzyme inhibition, and reduced transcription of several key genes. It has been shown that the antimicrobial effect of CNTs strongly depends on their diameter, length, aggregation degree, concentration, surface functionalization, degree of purification, and time and intensity of contact. The possibilities of the CNT biodegradation by microorganisms have been studied. It has been shown that the introduction of nanotubes into soils results in changes in the abundances of bacteria of certain taxonomic groups involved in biogeochemical cycles of carbon and nitrogen. This may adversely affect the cycling of these elements in the nature. The review also focuses on recent trends in the development of microbial fuel cells, biosensor technologies, bioremediation, and wastewater treatment in which CNTs display their unique electron-conducting and adsorption properties and serve as a bridge for an understanding of the beneficial aspects of microorganisms.

Keywords: carbon nanotubes, microorganisms, antimicrobial action, bioremediation, biosensors, microbial fuel cells

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INTRODUCTION

The discovery of carbon nanotubes (CNTs) was one of the most significant achievements of science in recent decades [1]. Carbon nanomaterials have a set of exceptional structural and functional properties: high electrical and thermal conductivity, peculiar magnetic properties, significant tensile strength, outstanding specific surface area, and chemical stability [2, 3]. Due to their unique physicochemical properties, CNTs find applications in various areas of human economic activities—electronics, mechanics, and power generation, as well as, recently, in biomedicine, biotechnology, and biosensor technologies.

The development and widespread use of new materials inevitably raises the question of their impact on living organisms. The first priority is to assess the risks of spreading nanoscale materials and their effects on human health. The impact of nanoobjects on the organism as a whole definitely begins at the cellular level, and that is why an understanding of their interaction with single-celled organisms is very important. Moreover, among living organisms, microbes, especially bacteria, are closest in size to nanomaterials, which ensures the possibility of their direct contact.

The current state of biotechnology implies the use of nanomaterials (including carbonaceous materials) for different purposes, such as energy generation by microbes, environmental clean-up, and biosensory technologies. All of these applications raise the question of CNT compatibility with single-celled living organisms.

Thus, the problem of interaction of microorganisms with CNTs can be considered in several aspects. On the one hand, nanomaterials can be used as new antimicrobials (with bacteria, microfungus, and algae serving as test objects to study the nanomaterial toxicity). At the same time, CNTs can serve as adsorbents for microorganisms in water purification and contaminant biodegradation and as an electron-conducting material in microbial fuel cells and biosensors (Fig. 1). This review summarizes the data from recent years on the results of studies related to the interaction of microorganisms with single-walled CNTs (SWCNTs), multiwalled CNTs (MWCNTs), functionalized CNTs (FCNTs), and nonfunctionalized CNTs; the mechanisms of the toxic CNT action on microorganisms;

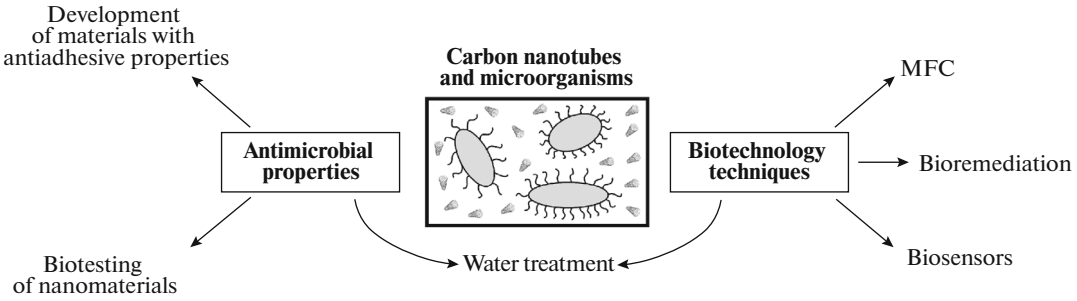

Fig. 1. Interaction between microorganisms and CNTs.

and the application of carbon nanomaterials in biotechnologies based on beneficial aspects of microorganisms.

CNT EFFECTS ON MICROORGANISMS

As early as 1943, long before the development of technology for the synthesis of carbon nanomaterials, Zobell [4] assumed that bacteria could be adversely affected by objects of a smaller size. However, even now, despite the large number of scientific papers on microbial interaction with CNTs, it is not possible to confirm or reject this hypothesis fully. The overwhelming number of published works verify the cytotoxic effect of these nanomaterials (Table 1). However, contradictory results were also reported. For a better understanding of this issue, we must separately investigate the effects of SWCNTs, MWCNTs, FCNTs, and NFCNTs at the cellular and population-based levels.

Antimicrobial effects. The first evidence of the strong antimicrobial activity of purified SWCNTs was reported in [5]. The authors demonstrated that the antimicrobial action of SWCNTs was associated with cell membrane damage in the model organism *Escherichia coli* K12 via direct contact, which resulted in bacterial cell death. Scanning electron microscopy (SEM) images showed morphological changes in *E. coli* K12 cells (incubated with SWCNTs for 60 min), which are attributable to loss of cellular integrity. Also, a more than fivefold increase of plasmid DNA and a twofold increase of RNA in solutions after cellular exposure to SWCNTs verified the efflux of cytoplasmic materials. Fluorescent-based assays (cells were stained with DAPI fluorescent dyes and propidium iodide) showed that the cells on CNTs aggregates exhibited a substantial loss in viability, whereas the suspended free-swimming cells in the presence of SWCNTs exhibited no loss in viability as compared to the control.

These results raised a question: What is more toxic to bacteria—SWCNTs or MWCNTs? It would be reasonable to assume that, if the toxicity mechanism of CNTs implies bacterial cell damage via direct contact with CNTs, then the CNT diameter is a key factor in the inactivation of bacteria cells and, thus, SWCNTs should be much more toxic to bacteria. This assumption was verified by a fluorescent dye technique and SEM imaging of cells incubated with SWCNTs and MWCNTs. The much higher cytotoxicity of SWCNTs was shown not only by the cell damage but also by alterations in the expression of stress-related genes. The enhanced cytotoxicity of SWCNTs may be attributed to the larger surface area available for contact with a cell surface, their better penetration of the cell wall due to their smaller diameter, and their unique chemical and electronic properties [6].

The antimicrobial effect of SWCNTs in suspensions of the genetically modified *E. coli* strain K12 TG1 (p*lux*) carrying the cloned *lux* operon from luminiscent marine bacteria *Photobacterium leiognathi* was verified by morphological and physiological studies and direct inoculation. Atomic force microscopy (AFM) revealed the disruption in cell morphology, which was preceded by a twofold increase in the oxygen consumption rate after 2–3 h of cellular exposure to SWCNTs, along with a simultaneously decrease in the bioluminescence intensity of the cells (to 60% of the control level) and a decreased CFU count [7].

AFM observations confirmed that dispersed SWCNTs exhibit strong antibacterial activities against both Gram-negative *E. coli* and Gram-positive *Bacillus subtilis*. SWCNTs are capable of developing nanotube networks on the cell surface, which then destroy the cell envelopes, leading to the subsequent leakage of intracellular contents and a decrease in cell volume and height. Furthermore, when the cell exposure time to SWCNTs is increased, the cell surface roughness increases [8]. These data correspond to previous studies by these authors, who showed that 58% of *E. coli* and 87% of *B. subtilis* cells died after 2 h of incubation with SWCNTs, and SEM images showed that the cells were seriously damaged. Thus, the antibacterial activity of SWCNTs results from the accumulation of interactions of a large amount of nanotubes in the form of a network on the surface of bacterial cells.

Longer SWCNTs exhibited a more pronounced antibacterial activity due to their more effective aggregation with microbial cells, whereas shorter ones tended to self-aggregate [9].

Table 1. Antimicrobial action of carbon nanotubes

Type of nanotubes	Microorganism	Effect and mechanism of action	Reference
SWCNTs	*E. coli* K12	Cell membrane damage, efflux of cytoplasmic contents	[5]
SWCNTs	*E. coli* K12 TG1 (p*lux*)	Morphological damage in cells, increased oxygen consumption rate, decreased bioluminescence intensity of cells (up to 60% of the control level)	[7]
SWCNTs	*E. coli*, *B. subtilis*	Cell wall damage, leakage of intracellular contents, decreased cell volume and height, enhanced bacterial surface roughness	[8]
SWCNTs with metallic properties	*E. coli*	Increased content of oxidized glutathione in cytoplasm; oxidative stress	[14]
Low purity SWCNTs	*E. coli*	Damage in cell surface structure	[29]
SWCNTs; carboxylated SWCNTs; MWCNTs	*E. coli*, *Ochrobactrum* sp.	Increased fluidity of bacterial cytoplasmic membrane, an increased level of saturated fatty acids and a simultaneously decreased level of unsaturated fatty acids	[32]
SWCNTs-OH	*Paracoccus denitrificans*	Inhibition of key glycolic enzymes, decreased NADH formation, decreased activity of nitrate reductase	[51]
SWCNTs-OH; SWCNTs-COOH	*P. denitrificans* ATCC 19367	Decreased transcription of key genes involved in substance transport, electron transfer, and transcriptional regulation; expression modulation of key genes involved in the glycerolipid/ free fatty acid cycle	[52]
SWCNTs, short and long MWCNTs, short MWCNTs-OH and MWCNTs-COOH	*Lactobacillus acidophilus, Bifidobacterium adolescentis, E. coli, Enterococcus faecalis, S. aureus*	"Piercing" with short SWCNTs, "wrapping" with long MWCNTs, damage in cell walls and membranes, loss of membrane potential, DNA and RNA release	[39]
SWCNTs, SWCNTs-COOH, MWCNTs	*Dyella ginsengisoli* LA-4	"Piercing," oxidative stress	[67]
MWCNTs/lysine, MWCNTs/arginine	*E. coli, S. typhimurium, S. aureus*	Electrostatic adsorption on the bacterial cell wall, loss of viability	[17]
Functionalization of MWCNTs with surfactants	*S. mutans*	Bacterial aggregation, loss of viability	[16]
Covalent immobilization of cephalexin *via* PEG on MWCNTs	*E. coli, P. aeruginosa, S. aureus, B. subtilis*	Effective adsorption of bacterial cells, loss of viability	[20]
FMWCNTs with carboxylic, phenolic groups, and 1-octodecanol and impregnated with silver nanoparticles modified with dodecylamine	*E. coli*	Aggregation, loss of viability	[22, 23]

SWCNTs exhibit a pronounced antibacterial activity against both suspended and adhered bacteria and affect biofilm formation [10]. However, the authors [11] found that SWCNTs did not exhibit an antibacterial effect against *Bacillus anthracis* spores. This is not surprising, in light of the thick protective coat of bacterial spores and the mechanisms of bacterial cell inactivation by this type of CNTs. At the same time, SWCNTs possess intrinsic properties that can be used to enhance their antibacterial activity. Since they absorb the light in the range of 700–1100 nm and then convert it into heat, the continuous near-infrared radiation on

spores treated with SWCNTs can induce cell death due to strong local heating [11]. These studies were natural continuations of earlier works showing the high adsorption affinity of SWCNT aggregates towards *B. subtilis* spores, which serve as a nonpathogenic model of *B. anthracis* [12].

The development of antimicrobial photodynamic therapy is a promising non-antibiotic approach to microorganism inactivation. An amine-functionalized porphyrin conjugated to the oxidized SWCNTs induced cell membrane damage in *Staphylococcus aureus* in visible light. This approach can be an alternative to the conventional treatment of localized infections [13].

One work [14] has shown that a key factor that determines the antibacterial activity of SWCNTs is their electron transfer properties, namely, whether they exhibit the properties of a metal or a semiconductor. A more pronounced loss of *E. coli* viability was observed with an increased fraction of metallic SWCNTs. The increased oxidized glutathione content in the cells exposed to such SWCNTs indicated oxidative stress. The authors postulated a three-step antimicrobial mechanism of the SWCNT action: (1) SWCNT contact with the bacterial surface; (2) their action on the cell membrane; and (3) oxidative stress.

The authors [15] proposed a scheme based on the interaction between nanotubes and enzymes as a possible molecular mechanism of SWCNT toxicity to microorganisms. SWCNTs cause significant conformational changes in microbial enzymes, including global changes, which lead to more or less dense molecular packing, and local changes that result from the filling of cavities, which are active sites. Furthermore, SWCNTs induce changes in the self-interaction of proteins, which affects the cellular metabolism.

Antimicrobial effects of MWCNTs. MWCNTs are presumably less toxic to bacteria than SWCNTs [5, 10, 16–19]. Although MWCNTs also effectively cover the bacterial cell surface, they do not exhibit an antibacterial effect due to their larger diameter as compared to SWCNTs [16]. The reduced toxicity of MWCNTs may result from the looser interactions between bacteria and nanotubes due to the higher rigidity of MWCNTs and possibly smaller van der Waals forces on their surface. For the same reason, MWCNTs of a smaller diameter exhibited a higher cytotoxicity. When MWCNTs are uncapped, short, and dispersed in the solution, their toxicity to microorganisms increases [10].

One method to increase the antibacterial activity of MWCNTs is their functionalization. CNTs can be modified by covalent and noncovalent functionalization, but noncovalent is preferable in order to preserve the nanotube structure and properties. In the case of noncovalent functionalization, the modifying molecules are adsorbed on the outer surface of nanotubes through hydrophobic forces or π-π stacking interactions, or through electrostatic interactions if an ionic adsorbate is used [16]. Compounds of different natures can be used as modifying agents. For example, the cytotoxicity to bacteria significantly increased when MWCNTs were functionalized with arginine and lysine. Their antibacterial activity increased in the order nonmodified MWCNTs–MWCNTs/lysine–MWCNT/arginine. Although the functionalized MWCNTs (FMWCNTs) were mainly effective against Gram-negative bacteria, such as *E. coli* and *Salmonella* Typhimurium, the antimicrobial activity of these CNTs against antibiotic-resistant strains of *Staphylococcus aureus* was also observed. The authors have assumed that the enhanced antibacterial activity of such FMWCNTs is associated with a positive charge on the surface of their functional groups, which ensures effective electrostatic adsorption on the bacterial cell wall [17].

The surfactant-modified MWCNTs also exhibited strong antimicrobial effects. The absorbed surfactant molecules on the surface of MWCNTs enhanced the dispersing power of the latter in the aqueous media, thus, increasing the binding capacity of MWCNTs to bacteria. The antibacterial activity of these FMWCNTs against *Streptococcus mutans* depended on the nanotube concentration and incubation time [16].

Covalent immobilization of the antibiotic cephalexin via a poly(ethylene glycol) (PEG) linker improved the antimicrobial properties of MWCNTs against Gram-negative *E. coli* and *Pseudomonas aeruginosa*, Gram-positive *S. aureus,* and *B. subtilis,* and it reduced the adhesive capacity of these bacteria. This occurs because MWCNTs are capable of adsorbing bacterial cells, which form biofilms on accessible surfaces. The antibacterial and anti-adhesion properties of FMWCNTs might be useful in biomedical materials and coatings [20]. In addition, the authors [21] imply that the use of FCNTs as antibiotic carries will ensure targeted delivery and enhance the bioavailability of antibiotics, and it will result in a decrease in the associated resistance of microorganisms.

A method for the removal of *E. coli* from aqueous solutions was patented in the field of water disinfection. The method consists of the mixing of a bacterial suspension with MWCNTs functionalized with carboxylic, phenolic groups, and 1-octodecanol or impregnated with silver nanoparticles [22]; it is modified with a dodecylamine group [23]. The method is based on the antibacterial properties of FMWCNTs and their ability to form aggregates with bacteria.

Thus, the effect of carbon nanomaterials is primarily based on the loss of the cellular integrity. Experimental studies have shown that nanomaterials are adsorbed on the bacterial membrane at the first stage of their interaction with bacteria; they then penetrate the membrane, extract lipids, induce pore formation, or activate membrane receptor proteins [24].

How unambiguous is the statement on CNT cytotoxicity towards microorganisms? Modern studies on the

interaction of microorganisms with CNTs do not give a clear answer to the question on the antimicrobial action of these nanomaterials. For example, MWCNTs in the concentration of 2 to 40 μg/mL did not affect the viability of *Saccharomyces cerevisiae* [25]. A producer of bacterial cellulose, *Gluconacetobacter xylinum*, was incubated under constant agitation with PEG-functionalized MWCNTs dispersed in culture media. The results of confocal microscopy confirmed the presence of living bacteria in the media, and SEM images showed a significant amount of well-dispersed MWCNTs attached to the surface of cellulose fibers [26]. It was also assayed via a CFU count, and cell staining with Live/Dead® fluorescent dye showed that the viability of *Alcaligenes faecalis* 2 and *Rhodococcus ruber* gt1 remained unchanged after exposure to either purified or containing process-related impurities MWCNTs introduced into culture media [27]. Quantitative diffusion was used in a study [28] in which SWCNTs (1 mg) were added to the surface of an agarized media inoculated with bacteria such as *S. aureus, B. cereus, S. epidermidis, Streptococcus pyogenes, E. coli, S.* Typhimurium*, Proteus* spp.*,* and *P. aeruginosa*. The inhibition zone was detected only for *S. aureus* and *B. cereus*.

Atomic force microscopy (AFM), the most preferable method for the study of single cell morphology, does not give clear evidence of CNT toxicity. Thus, Deryabin, et al. found that the interaction of MWCNTs and several SWCNTs with the *E. coli* surface did not induce any morphological or viability changes in bacterial cells. The authors revealed that only low-purity SWCNTs caused damage to the cell surface structure [29].

The MWCNT–cell contact did not significantly increase the number of revertant colonies in the bacterial test system. Thus, it was concluded that these carbon nanomaterials have no mutagenic effects on bacteria [28, 30].

Recent studies on the interaction between microbial cells and CNTs have shown that the antibacterial activity of CNTs is influenced by many factors, including their diameter, length, aggregation degree, nanomaterial concentration, surface functionalization, and purification degree, as well as the used buffer solution and contact time and intensity [8, 16, 31–33]. Electrostatic interactions between positively charged CNTs and the negatively charged surface of bacteria lead to the aggregation of bacterial cells with nanotubes. Both SWCNTs and MWCNTs exhibit cytotoxicity to microbial cells. The mechanism of SWCNT toxicity probably involves direct damage to the bacterial cell wall, whereas MWCNTs are capable of inducing oxidative stress in the cell [34]. Although other possible mechanisms of toxicity are also being considered (such as the inhibition of electron transport, increased cell membrane permeability, and the generation of reactive oxygen species), most of these mechanisms have not yet been proven experimentally. It was shown that increased CNT concentrations (such as MWCNTs, long and short SWCNTs, short carboxylated SWCNTs) increased the cytoplasmic membrane fluidity of bacteria. The authors observed a significant negative correlation between the viability and membrane fluidity of *E. coli* and *Ochrobactrum* sp. Furthermore, the authors observed an increased level of saturated fatty acids and a decreased level of unsaturated fatty acids, which was an adaptive response of bacteria exposed to CNTs [32].

The influence of CNTs on biofilm formation is also not clear. On the one hand, the antimicrobial properties of nanotubes prevent from bacterial adhesion and biofilm formation [35, 36]. However, on the other hand, the biofilm formation is known to occur on such materials as well. In this case, the dead cells on the material surface protect living bacteria from the toxic action of CNTs, which results in "live-on-dead" biofilm formation [33, 37].

Most studies pay attention to the morphological changes in cells exposed to CNTs detected by AFM and SEM. However, this is not enough to understand physiological changes. Studies in transcriptomics and proteomics and systemic biological approach are required to clarify the causes and mechanisms of cell death [38].

It was experimentally proven that the antibacterial effect of CNTs increases as the nanotube diameter decreases and, therefore, that SWCNTs are more toxic to microorganisms than MWCNTs [5, 6, 16–19] and long SWCNTs are more toxic than the short ones [9], whereas short MWCNTs are more toxic than the long ones [10]. Functionalized, unpurified, and exhibiting metallic properties CNTs exhibit a stronger antimicrobial effect [14, 16, 17, 20, 21, 27, 29]. CNT cytotoxicity is usually dose-dependent [16, 38, 39]. Therefore, the contradictory results on the cytotoxicity of CNTs require standardization of the applied methods and unification of the approaches for the detection of their antimicrobial activity.

CNT EFFECTS ON ECOSYSTEMS

CNT effects on the composition of microbial communities of soils and bottom sediments. The use of CNTs in different sectors of the national economy, electronics, medicine, and biotechnologies will lead to increased production of CNTs and, respectively, to their increased release into the environment. Moreover, according to the available data, carbon nanomaterials have great potential as regulators of plant growth [40–42]. The issue of environmental impacts of new materials requires clarification of their action on microorganisms, which are essential in the cycling of biogenic elements in biosphere.

In a 90-day experiment, the authors of [43] studied the impact of various concentrations of MWCNTs,

from low (10 mg/kg) to extremely high (10 000 mg/kg), on the microflora of sandy loamy soils. The extremely high MWCNT concentrations led to a shift in the composition of microbial communities: the abundance of bacterial genera *Derxia, Holophaga, Opitutus,* and *Waddlia* decreased, while the abundance of *Rhodococcus, Cellulomonas, Nocardioides,* and *Pseudomonas* increased. It is interesting that the bacterial abundance increased for the typical degraders of such biologically recalcitrant contaminants as polycyclic aromatic hydrocarbons.

It should be noted that an increase in the abundance of microorganisms capable of degrading petroleum hydrocarbons was observed when freshwater sediments (contaminated with crude oil) were spiked with CNTs. The microbial diversity changed, and the most susceptible were *Flavobacteriales, Acholeplasmatales, Burkholderiales, Chlamydomonadales, Chlorellales, Chromatiales, Desulfovibrionales, Gemmatimonadales,* and *Myxococcales*. The abundance of the order *Actinomycetales* increased after exposure to crude oil mixed with CNTs. The authors assumed that the addition of MWCNTs to crude oil–contaminated media makes hydrocarbons much more accessible to microorganisms and enhances biomass growth [44].

Due to their adsorption properties, CNTs can affect the bioavailability and the toxicity of other organic contaminants. Thus, MWCNTs affect the composition of microbial communities of soils contaminated with polycyclic aromatic hydrocarbons, and the effect varies depending on the soil type and the organic matter content in the soil. Soil treatment with MWCNTs (50 and 100 mg/kg) dramatically changed the relative composition of microbial communities in sandy loam soils (1% organic matter) as compared to the control, but it did not affect that of sandy clay loam soils (5.9% organic matter). Nevertheless, treatment with MWCNTs (100 and 50 mg/kg) increased the pyrene biodegradation in sandy clay loam soils (by 21 and 9.34%, respectively) [45].

Another group of researchers compared the effects of nonmodified and functionalized MWCNTs (50, 500, and 5000 μg/g) on the soil microflora. It was noted that only FMWCNTs affected the composition of soil communities, apparently, because FMWCNTs are more capable of being mixed with the soil water. Furthermore, the more pronounced effect of FMWCNTs was associated with soil acidification after the introduction of the nanomaterials in large concentrations [46].

The introduction of MWCNTs (of 50–200 mg/L) changed the relative composition of the bacterial community in soil where tomatoes were grown, but the diversity and basic phylotypes remained unchanged. The introduction of 200 mg/L of MWCNTs increased the abundances of *Bacteroidetes* (from 33.1% in the control to 57.7%) and *Firmicutes* (from 1.9% in the control to 3.1%). Moreover, the increase in the bacterial abundances was prorated to the nanotube concentration. However, the abundances of *Proteobacteria* and *Verrucomicrobia* decreased from 50.3 to 28.3% and from 3.5 to 2%, respectively. At a nanotube concentration of 200 mg/L, the abundance of *Sphingobacteria* (phylum of *Bacteroidetes*) significantly increased from 8.2 to 24.7%, while the abundance of *Alphaproteobacteia* decreased from 39.3 to 22.7% [41]. Somewhat different results were obtained in studies of the MWCNT impact on the composition of bacterial communities in a rhizosphere of rice grown in a loamy potted soil. The researchers noted a decreased abundance of the dominant group, *Proteobacteria,* from 3.96 to 3.25% when the MWCNT content increased from 50 to 500 mg/kg. The abundance of *Gammaproteobacteria* decreased when the MWCNT soil content increased, whereas the *Alphaproteobacteria* abundance remained unchanged at all MWCNTs. The abundance of *Nitrospira* in soil decreased prorated to increasing the amount of MWCNT concentrations; therefore, CNTs can indirectly affect the soil nitrogen cycle [47].

The microbial enzyme activity also reflects the ecosystem status. The effect of MWCNTs [48] and SWCNTs [49] on the activity of soil enzymes, such as 1,4-β-glucosidase, cellobiohydrolase, xylosidase, 1,4-β-N-acetylglucosaminidase, and phosphatase was studied. Both MWCNTs and SWCNTs decreased the enzymatic activity, but SWCNTs exhibited an inhibitory effect at a fivefold lower concentration. The activity of most enzymes decreased when 500 μg/g of MWCNTs were introduced into the soil; the activity of all of the studied enzymes was completely suppressed at 5000 μg/g of MWCNTs, whereas only 300–1000 μg/g of SWCNTs inhibited the enzymatic activity and decreased the amount of microbial biomass [48, 49].

Both MWCNTs and SWCNTs had a significant impact on the diversity of the ammonia oxidizing bacteria and archaea in soils. Moreover, a single introduction of CNTs led to a drastic decrease in the archaea abundance, while the additional introduction of CNTs returned the relative abundance of these microorganisms to the initial values [50].

Hydroxyl-modified SWCNTs exhibited a strong inhibitory effect on denitrification. Studies with a *Paracoccus denitrificans* model microorganism showed that FSWCNTs inhibited key enzymes involved in glycolysis, which leads to a drastically decrease in NADH production (an electron donor for denitrification) and a decreased activity of nitrate reductase [51]. FSWCNTs were later shown to affect transcriptional regulation in denitrifying bacteria. Both hydroxylated and carboxylated SWCNTs exhibited a strong inhibitory effect on denitrification, but the effect of the former was much stronger. SWCNTs-OH had a much stronger effect on the expression of key genes related to the transport of substances, electron transfer, and transcriptional regulation, reducing it. It was shown that FSWCNTs modulate the expression of key genes

responsible for the glycerolipid–free fatty acid cycle and thus impairs denitrification-related processes, which include the energy and intracellular redox balance and transportation [52]. Thus, the release of a large amount of SWCNTs-OH in to the environment can lead to serious disruptions in the nitrogen cycle in the biosphere.

In general, it is essential to consider possible shifts in relative abundances of some certain taxonomic groups of soil bacteria under the action of CNTs, since changes in the composition of bacterial communities participating in biogeochemical cycles of carbon and nitrogen can adversely affect the cycling of these elements in the nature.

Effects of CNTs on the composition of microbial communities in an aquatic environment. The impact of CNTs on biological objects is also associated with their capacity for pollutant sorption, which is especially important in an aquatic environment. The action of SWCNTs and MWCNTs on microbial communities in an aquatic environment in the presence of Cu^{2+} and CrO_4^{2-} ions was found to differ from their action in the absence of metal ions and their oxides. The toxicity of CNTs significantly increased in the presence of metals, which can be explained by two possible mechanisms: first, CNTs can change permeability of the cell wall, allowing metals to penetrate it; secondly, CNTs adsorb metals for a certain time and simultaneously affect the cells while aggregating. *Bacillus* sp. and *Acidithiobacillus* sp. remained the dominant taxa under such conditions. CNTs modified with carboxyl and hydroxyl groups turned to be more toxic to microorganisms [53].

The CNT toxicity in an aquatic environment also depends on the availability of nutrients, since the ability of microorganisms to restore their disturbed vital functions in the presence of nanomaterials was dependent on cell nutrition [18].

The solids suspended in an aquatic environment can alter the CNT toxicity to microorganisms. The aggregation of suspended solids and SWCNTs apparently limited their accessibility to bacterial cells. Since the amount of such solid particles in the natural aqueous media is much higher than the SWCNT content, the role of the solids should be taken into account to assess more thoroughly the adverse effects of SWCNTs on aquatic microorganisms [54].

Studies of the impacts of nanomaterials on microbial communities of active sludge are very important, since a decreased efficacy of wastewater purification processes results in the discharge of untreated waste into the environment. The composition of microbial communities in active sludge changed even after short-term exposure to SWCNTs. SWCNTs were noted to have an adverse impact on the *Sphingomonadaceae* community, which plays an important role in xenobiotic degradation and flocculation. There is a low probability of direct contact between CNTs and microbial cells, since CNTs are incorporated in the extracellular polymer matrix, which protects the cells from direct action [55].

CNT degradation by soil microorganisms. Studies of the environmental properties of CNTs should consider their possible biodegradation. Tracer analysis indicated that microbial communities are capable of biodegrading MWCNTs in the presence of an additional carbon source. Among such bacteria capable of biodegrading MWCNTs are *Burkholderia kururiensis*, *Delftia acidovorans,* and *Stenotrophomonas maltophilia*. They decomposed MWCNTs to carbon dioxide and such intermediate products as 2-methoxy naphthalene, 2-naphthol, cinnamaldehyde, and isophthalic acid [56].

The hydrocarbon-degrading strain *Mycobacterium vanbaalenii* PYR-1 can decompose both nonfunctionalized and carboxyl-functionalized MWCNTs; the latter are degraded at a higher degradation rate. During 25 days of strain growth on media containing glucose or glucose and pyrene, morphological changes were observed in both types of CNTs: MWCNTs became shorter and thinner with a highly disordered tubular structure with kinks, bends and broken ends. The degradation apparently occurred via the oxidation of crystal lattices and the subsequent exfoliation of graphite walls. The authors [57] assume that carotenoids in mycobacteria may protect them from the oxidative stress induced by MWCNTs.

Thus, a question arises as to means by which CNTs are exposed to degradation by microorganisms. The basic CNT structure consists of aromatic rings connected to each other by sp^2-hybridized carbon atoms. This structure is similar to polycyclic aromatic hydrocarbons and is stable. However, pentagon-heptagon pairs known as Stone–Wales defects, sp^3-hybridized carbon atoms, and open ends make CNTs more chemically active [58] and easily accessible to enzymatic attacks.

The nanomaterial-resistant soil bacteria *Trabusiella guamensis* mediated the biotransformation of MWCNTs via surface oxidation. Nevertheless, the structural transformations in MWCNTs under the action of microorganisms are still unclear [59].

Fungi are also capable of CNT biodegradation. Thus, *Sparassis latifolia* secretes lignin-peroxidase, which participates in the biodegradation of thermally treated and thermally untreated SWCNTs [60]. Manganese-dependent peroxidase from the white-rot *Phanerochaete chrysosporium* is capable of decomposing nonfunctionalized SWCNTs [61].

The results concerning CNT degradation allow us to conclude that, first, the surface modification or functionalization of CNTs may either enhance or inhibit their biodegradation, and biodegradation therefore depends on the properties of the used modifiers. Second, the potential of microbial communities in of nanomaterial biodegradation is much higher than of pure microbe cultures. In addition, the environ-

ment may be contaminated not with CNTs but with graphene and its derivatives; therefore, it is important to explore the possibility of their combined biodegradation [61].

CNTs can hardly be considered easily degradable materials, since there are still very little data on their biodegradation and biotransformation with microorganisms. This is associated not only with the stability of the CNT structure. Since CNTs emerged only lately, the environmental microflora requires time to adapt to these new man-made carbon nanostructures.

CNT APPLICATIONS IN BIOTECHNOLOGIES

The main areas of CNT applications in biotechnologies include water treatment based on the sorption properties of nanotubes (i.e., their ability to concentrate and remove bacteria and, at the same time, to serve as a carrier of microorganisms capable of biodegrading pollutants); microbial fuel cells (MFCs) (which use important CNT features such as high electrical conductivity); biosensors (in which nanotubes are applied as a carrier of microbial cells and an electron-conducting substrate).

In the field of environmental biotechnologies, CNTs can be used for two seemingly opposite purposes: firstly, biofouling prevention (by blending nanotubes exhibiting antimicrobial properties with composite materials or CNT deposition on the surface of various materials, pipelines, filters, etc.); second, facilitation of the formation of the required biofilms on a substrate of CNTs with reduced cytotoxicity [35]. The hydrophobic/hydrophilic properties of composite materials can be altered with the use of different compounds for CNT functionalization, which makes the surface either protected from microbial adhesion and biofilm formation or, alternatively, more preferable for biofilm formation [62].

CNTs in water treatment and bioremediation technologies. Due to their aggregation capacity, CNTs can be used in the removal of biocontaminants (bacteria and viruses) from wastewater. In contrast to activated carbons, nanotubes are not only capable of adsorbing bacteria, but they also contribute to pathogen detoxication due to their intrinsic antimicrobial properties. The smooth surface of Gram-positive bacteria cells makes these bacteria more susceptible to CNTs than Gram-negative bacteria. The dispersion of CNTs in solution, with increases in their concentration and agitation rate during incubation, may lead to enhancement of the induced effect of cell wall damage [38].

Membrane filtration is one of the most effective methods for the removal of bacteria and viruses from water and waste. However, the wider application of membrane technologies is limited due to biofouling of the membrane surfaces. CNT-containing composite membranes are more resistant to biofouling [63]. Water ultrafiltration membranes consisting of vertically aligned nanotubes have been developed. Such millimeter-thick membranes provided a water permeability of 30000 L m^{-2} h^{-1} bar^{-1} and were resistant to biofilm formation on their surface [64].

Some scientific papers have shown that CNTs affect the pollutant biodegradation in various media [65–68]. Thus, unmodified and oxidized MWCNTs influenced the atrazine (a chlorotriazine herbicide) degradation rate induced by Actinobacteria *Arthrobacter* sp. The biodegradation rate increased by 20% at a nanotube content of 25 mg/L, while it decreased by 50% at the nanotube content of 100 mg/L. The stimulating effect of low MWCNT concentrations was induced by enhanced bacterial growth and overexpression of degradation genes. CNTs either stimulated or inhibited the biodegradation due to the combination of two different effects: their toxic action on microbial activity and changes in the bioaccessibility of degraded substances that resulted from the sorption–desorption processes [66].

The CNT effects on the growth in *Dyella ginsengisoli* LA-4 and biphenyl biodegradation by these bacteria were concentration-dependent. The cell growth and biphenyl degradation were enhanced at a 1–1.5 mg/L concentration of MWCNTs or carboxylated SWCNTs. CNTs aggregated and adsorbed cells and biphenyl, creating a suitable microenvironment for cell proliferation in which bacteria could easier utilize this organic pollutant [67].

The aggregation of CNTs with *Ralstonia solanacearum* in water media ensured the effective removal of microcystins (cyanobacterial toxins). *R. solanacearum* was capable of biodegrading microcystins, and CNTs (even when diluted with a large amount of water) adsorbed a significant amount of this substance and facilitated the aggregation of bacteria as acting as biodestructors, thus, increasing the process efficacy [65].

The uranium tolerance in *Bacillus mojavensis* cells (which are capable of accumulating uranium) immobilized on MWCNTs increased by almost seven times as the biosorption capacity reached 25.8 mg/g. The immobilized biosorbent column could be reused for at least 30 biosorption–desorption cycles [69].

Furthermore, CNTs may be used as a carrier for bacterial cell immobilization in biocatalytic technologies. Thus, the cells of *R. ruber* gt1, *R. erythropolis* 11-2, and *A. faecalis* 2 immobilized on MWCNTs were used to prepare a heterogeneous biocatalyst for the conversion of nitriles to amides and amides to the corresponding carboxylic acids. The preservation of nitrile hydratase and amidase activity of bacteria was shown [27].

Microbial fuel cells (MFCs). MFC is an electrochemical device that drives electricity generated by the microbial cell biomass. The main difference from other fuel cells is that an MFC uses a biocatalyst consisting of electrogenic microorganisms (bacteria or

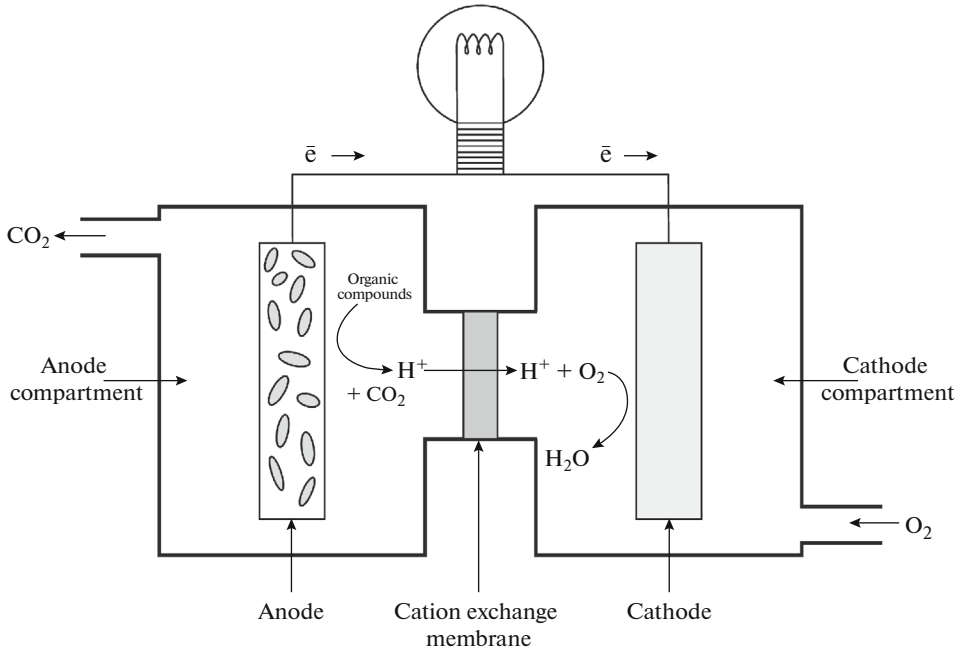

Fig. 2. Scheme of MFC.

algae) applied to the anode surface. A typical MFC consists of anode, cathode, membrane, and current collectors (Fig. 2). The development and use of MFCs have recently attracted much interest due to their ability to generate electrical energy from organic waste and biodegradable feedstock. However, the wider commercial use of this technology is limited by the low catalytic activity of microorganisms and costly construction materials. In the past decade, MFC efficiency has been significantly improved with the use of novel materials, which improve the achievable power density. This mainly applies to the use of nanomaterials in anode construction [70].

A number of scientific papers studied the potential application of CNTs to increase conductivity in MFCs [71–78]. The electrode composition may include both nonfunctionalized CNTs [75] and FCNTs or different nanomaterial composites [76–78]. The amine-terminated nanotubes functionalized with ionic liquids improved the interphase transfer of electrons from *Shewanella putrefaciens* cells immobilized on the anode in an MFC. The use of such composites not only improved the adhesion of the *S. putrefaciens* cells but also promoted both flavin-mediated and direct electronic transfer between the bacterial cells and the anode. This anode achieved a threefold higher power density than that of the anode, which included unmodified CNTs, since the introduction of ionic liquids significantly increased the positive charge of nanotubes without changing their morphology [76].

A MWCNT/reduced graphene oxide-based composite (in which the embedded MWCNTs not only prevent the aggregation of graphene oxide layers but also act as a scaffold strengthening the bonds between the layers) has a 3D sponge-like structure with a large specific surface area, excellent biocompatibility, and a high electron transfer rate. Such an anode in an MFC based on *Shewanella putrefaciens* CN32 delivered a maximum power density of 789 $mW\,m^{-2}$, which is much higher than that of the anode from individual CNTs or reduced graphene oxide, and six times higher than that of anode from conventional carbon cloth [77].

The new technology of biological hydrogen production with microbial electrolysis cells (MECs) was developed based on MFCs. The key feature of this technology is the production of hydrogen from organic waste via microbial electrolysis. Microorganisms oxidize organic materials to carbon dioxide and release electrons and protons (transferring the electrons from the oxidative reactions to the anode and releasing protons into the solution). The hydrogen is generated at the cathode in the proton-electron interaction with a supply of additional voltage. The biocathode in the MEC can also be modified with CNTs. In particular, a polyaniline/MWCNT composite was used in the composition of a biocathode for the production of biohydrogen in a single chamber membrane-free MEC [79].

Biosensors. A microbial biosensor is an analytical device consisting of microorganisms coupled with a transduction element designed for the detection of a wide range of chemical contaminants due to changes in the respiration and metabolism in living organisms. Viable cells are able, either aerobically or anaerobically, to convert organic substrates into different end-products, such as carbon dioxide, ammonia, and acids

that can be easily detected by a variety of transducers. The advantages of microbial biosensors include adaptation to adverse environmental factors and prorated quantitative changes in the respiratory and metabolic activities in response to toxic substances; there is no need to use an expensive or time-consuming procedure to isolate intracellular enzymes. The main disadvantage of a whole cell sensor is the limited diffusion of the analyte through the microbial cell wall, which results in a slower response than that with enzymatic sensors. The bioavailability of a target contaminant for the cells can be increased by different methods, including physical techniques (freezing and thawing), chemical techniques (exposure to detergents, solvents), enzymatic techniques (the use of lysozyme) or enhancement of the surface area accessible to cell immobilization, e.g., with the use of nanomaterials, such as CNTs [35].

A large, specific surface area and good conductivity allow CNTs to act as an "electrical wire" between the redox center of enzymes and the electrode surface, which makes CNTs an excellent material for the construction of electrochemical biosensors [80]. The use of CNTs in the microbial biosensor technology is advantageous due to their higher electrical conductivity, better operational ability, and stability over a wider range of temperature and pH [35]. In addition, CNTs exhibit unique intrinsic optical properties, such as photoluminescence in the near infrared light and strong resonance Raman scattering. CNTs have a low autofluorescence background and are almost insensitive to photobleaching as compared to organic dyes, which makes CNTs excellent candidates for biodetection [81, 82].

In [83], a bioelectrode based on Nafion (perfluorinated ion exchange resin)/*E. coli* BL21 (DE3) (bacteria expressing xylose dehydrogenase on the cell surface)/MWCNTs was developed. Such a biosensor was highly sensitive to D-xylose, exhibited no interference from other saccharides, and had a low detection limit to the analyte (0.5 μmol), good long-term stability, and reproducibility of the response.

Bacteria can be not only a biosensor element but also an analyte. A selective and sensitive biosensor based on MWCNTs functionalized with carboxyl groups immobilized by the antimicrobial peptide clavanin A was developed to detect Gram-positive and Gram-negative bacteria. This biosensor was used for the detection of *Klebsiella pneumoniae, Enterococcus faecalis, E. coli,* and *B. subtilis* [84]. A glassy carbon disc electrode modified with MWCNTs ensured rapid quantification of enterotoxigenic *E. coli* F4 (K88) (ETEC F4) without any sample pretreatment [85]. The authors [81] used bacteriophage M13-functionalized SWCNTs as probes for the recognition of F^+ and F^- bacterial strains. Moreover, with a one-step modification, they attached antibodies against certain bacteria to such FSWCNTs and elaborated a procedure to detect *S. aureus* intramuscular infections. Biofunctionalized aqueous-dispersed probes based on SWCNTs can potentially be used in studies of bacterial infections in the body, e.g., endocarditis [81].

Aptamers are short, single-stranded oligonucleotides that can effectively bind molecules of different nature with high affinity [86]. Aptamers can be used as molecular receptors in biosensors of different types. For example, electrochemical biosensors were developed to detect *Salmonella* Typhimurium. In particular, a linear response in the range from 0.2 to 10^3 CFU mL^{-1} was displayed by the interaction between the type IVB pili of salmonella and SWCNTs functionalized with RNA aptamers. In addition to electrochemical biosensors, the optical biosensors based on the surface plasmon resonance were used to detect *P. aeruginosa, S.* Typhimurium, and *Lactobacillus acidophilus* [87]. The development of a new generation of potentiometric aptasensors based on CNTs is very promising. Aptamers are capable of self-assembly via π-π stacking interactions with CNTs. The presence of target bacteria induces conformational changes in aptamers, leading to the separation of phosphodiester groups ionized at a pH of 7.4 from the surface of SWCNTs, to a change in the SWCNT charge, and the subsequent change in the recorded potential. Such aptasensors enable the real-time detection of analytes at ultra-low concentrations [88]. A nanosensor device was fabricated with the use of a noncovalent conjugation of a polynucleotide aptamer to near-infrared emissive SWCNTs. The efflux of unlabeled GTPase RAP1 and HIV integrase proteins from *E. coli* and *Pichia pastoris* immobilized in a microfluidic chamber was studied [89].

Thus, the use of carbon nanotubes in biotechnology is very promising, especially in the biodetection techniques and alternative energetics.

CONCLUSIONS

The application area of CNTs is continuously growing. The unique adsorption and electron-conducting properties of these nanomaterials can serve as the basis for bioremediation, biofuel production technologies, alternative energetics, and biosensor construction. Their cytotoxicity to microorganisms strongly depends on the interaction conditions between CNTs and microbial cells, the CNT type, and their functionalization, concentration, and morphological characteristics. Depending on the goals, the appropriate conditions could be selected and/or specific modifications of CNTs could be made that allow these nanomaterials to serve opposite purposes, including both the antimicrobial activities and utilization of the beneficial effects of microorganisms. The creation of new CNT-based composites will solve different problems, including biofouling, wastewater treatment, and the creation of biocompatible devices of improved performance.

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COMPLIANCE WITH ETHICAL STANDARDS

The authors declare that they have no conflict of interest. This article does not contain any studies involving animals or human participants performed by any of the authors.

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