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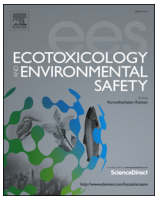

Review

Effects of carbon nanotubes on biodegradation of pollutants: Positive or negative?

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ABSTRACT

Recently, a large quantity of carbon nanotubes (CNTs) enters the environment due to the increasing production and applications. More and more researches are focused on the fate and possible ecological risks of CNTs. Some literatures summarized the effects of CNTs on the chemical behavior and fate of pollutants. However, little reviewed the effects of CNTs on the biodegradation of pollutants. In general, the effects of CNTs on the biodegradation of pollutants and the related mechanisms were summarized in this review. CNTs have positive or negative effects on the biodegradation of contaminants by affecting the functional microorganisms, enzymes and the bioavailability of pollutants. CNTs may affect the microbial growth, activity, biomass, community composition, diversity and the activity of enzymes. The decrease of the bioavailability of pollutants due to the sorption on CNTs also causes the reduction of the biodegradation of contaminants. In addition, the roles of CNTs are controlled by multiple mechanisms, which are divided into three aspects i.e., properties of CNTs, environment condition, and microorganisms themself. The better understanding of the fate of CNTs and their impacts on the biochemical process in the environment is conducive to determine the release of CNTs into the environment.

1. Introduction

In the past decades, the environment and the ecology problems are increasingly outstanding. A variety of contaminants from natural or artificial resources will threaten human health and environmental security (Sarkar et al., 2018). Therefore, it is essential to take some measures to deal with these problems. Conventional technologies for cleaning up the contamination can be divided into physical, chemical and biological methods, such as adsorption/reduction, filtration, biological mineralization, oxidation/precipitation (Liu et al., 2017; Yang et al., 2018). Among of various ways, the biological methods should be environmentally friendly, low-cost and less hazardous by-product way to remove environmental pollutants, especially for organic matters (Liu et al., 2018b; Shao et al., 2017). The efficiency of biodegradation can be affect by many factors, such as the condition for microbial growth and reproduction and the degree of refractory degradation of pollutants etc. Some factors can impact microbial properties while the others can influence the transport of contaminants to the microorganisms (Huang et al., 2016).

some exogenous chemicals can also increase or decrease biodegradation of contaminants. In the past five years, some papers have reported the effects of various chemicals on biodegradation. Among them, researches on the effects of carbonaceous materials on biodegradation is dominant. It is due to that the toxicity of carbonaceous materials to microorganisms and effects on biodegradation should be considered before they are used in remediation and wastewater treatment. As one of the most widely used carbonaceous materials, publications about effects of CNTs on biodegradation take up a great proportion (Fig. 1). CNTs are quite promising nanomaterials with superior physic-chemical properties, which have received great attention owing to their widespread application. For example, CNTs possess excellent sorption capability due to the large surface area. It makes them be used as adsorbents for removing contaminants in environmental (Hua et al., 2017; Yang et al., 2017). Besides, CNTs can also be found in other fields, such as biomedicine and biosensor (De Volder et al., 2013; Landry et al., 2017; Shamay et al., 2018). With increasing applications

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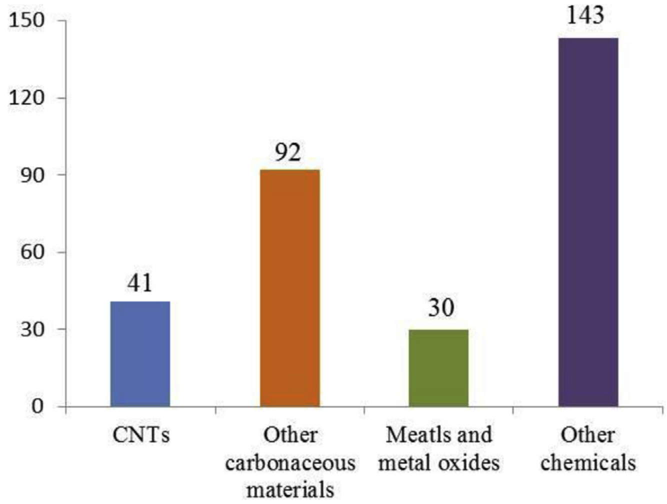

Fig. 1. Publication about biodegradation affected by various chemicals in past five years (2015–2019) (Source: Web of Science).

and production, CNTs are released into the natural environment as aggregates, composite particles, or dispersions by accident and direct acting. For example, CNTs could be released during the whole life cycle of polymer nanocomposite. The manufacture, use and disposal of CNTs-incorporated nanocomposite have the potential to release CNTs. Nanocomposite can also release engineered nanoparticles including CNTs during incineration or accidental fires (Petersen et al., 2011). The concentration of CNTs in the soil has reached 0.01–3 μg kg^{-1}. And due to contaminated surface water, the concentration of CNTs in sediment has reached 0.8 μg kg^{-1}(Chen et al., 2016, 2017a Glomstad et al., 2016a). So it is inevitable for living organisms and human exposed to CNTs. Some studies about the multifarious effects of CNTs to human and environment have been reported (Amiri et al., 2016b). It is not hard to image that CNTs might also have some effects on the biodegradation process. In fact, there are already some relevant researches published. However, little literatures reviewed the effects of CNTs on biodegradation of pollutants in environment.

Biodegradation is a feasible and common way to treat pollutants. It is beneficial to avoid the adverse effects of CNTs on biodegradation of pollutants and make full use of the excellent properties of CNTs. Besides, this is of great significance for environmental protection. CNTs may interfere with the biodegradation process by three approaches. Firstly, CNTs can change the biodegradation of pollutants by increasing or inhibiting microbial growth. Secondly, CNTs can adsorb the pollutants due to their excellent adsorption capacity. Subsequently, the biodegradation efficiency can be decreased with the decrease of bioavailability attributing to adsorption of CNTs. Thirdly, CNTs can interact with degradation enzymes thus affecting the biodegradation process (Glomstad et al., 2016b; Ming et al., 2017).The results of CNTs participated in the biodegradation process are often multifaceted. Although most of studies have been published on the negative effects of CNTs. CNTs have also been found to have positive effects on biodegradation in some cases. And the negative effects of CNTs can generally be regulated by various factors (Table 1).

In this review, previous studies related to the effects of CNTs on the biodegradation of pollutants were summarized, including effects on microorganisms, enzymes and pollutants. Versatile microorganisms react differently to CNTs with different properties. It depends on the properties of CNTs, the environment and the microbes themselves. Some microbial enzymes also have the function on degrading pollutants. Their activity can be affected by the addition of CNTs. Besides, the adsorption of pollutants by CNTs can also affect the biodegradation process, which is due to the change of bioavailability.

2. Effects of CNTs on microorganisms

2.1. Properties of microorganisms with addition of CNTs

2.1.1. Microorganisms in soils

After CNTs enter into environment, soil may become the final recipient of CNTs (Shrestha et al., 2013).Soil microorganisms can act as indicators of soil quality and govern the mineralization of pollutants and nutrient cycling (Hao et al., 2017). Owing to the accumulation of CNTs in soil, it is possible for CNTs disturbing microbial community and affecting some important microbial process including mineralization of pollutants. Soil microbial biomass is one sensitive indicator of contamination disturbance like heavy metals and nanomaterials. A number of studies showed that microbial biomass and microbial biomass C:N altered after exposure to CNTs. Jin et al. observed that microbial biomass C decreased with 300 μg powder form SWCNTs (single-walled carbon nanotubes)g^{-1}soil or more than 600 μg suspended form SWCNTs g^{-1}soil. High concentration of SWCNTs (600 μg g^{-1} soil and 1000 μg g^{-1} soil) also decreased microbial N and microbial biomass C:N (Jin et al., 2013). Chen et al. similarly showed that first exposure to SWCNTs (100,200,500 μg g^{-1} soil) or MWCNTs (100,500,1000 μg g^{-1} soil) had negative effects on biomass C. MWCNTs had minor effects than SWCNTs. Interestingly, 500 μg SWCNTs g^{-1} soil significantly increased microbial biomass C (Chen et al., 2015). Another research investigated the effects of MWCNTs on two types of soil. At both of site 1 and site 2, 5000 μg MWCNTs g^{-1} soil lowered microbial biomass C and N. However, no significant effects can be found with MWCNTs at concentration of 50 or 500 μg g^{-1} soil (Chung et al., 2011). In another study, except for 500 mg kg^{-1} soil of C_{60} (fullerene)increased the microbial biomass C, rGO (reduced graphene oxide) and MWCNTs had no significant effects on biomass C at 50 and 500 mg kg^{-1} soil (Hao et al., 2017).In general, it can concluded that the effects of CNTs on microbial biomass have an positive correlation with concentration. At moderate concentration, CNTs have no or little effects. When the concentration is high enough, CNTs may have negative effects on microbial biomass. However, these studies were conducted with CNTs in short incubation period. Tong et al. suggested the microbial biomass had no significant changes with repeated addition of SWCNTs after 6 week incubation (Tong et al., 2012). CNTs may affect microbial function by effects on specific microorganism population. Several studies investigated the effects of CNTs on microbial process like nitrogen cycle. Nitrogen cycle is a crucial microbial process and have significant relevance to water quality. Nitrification and denitrification play important roles on nitrogen cycle. In one research, at first exposure to CNTs, CNTs suppressed the net N nitrification. Afterward, CNTs stimulated the net N nitrification. However, in the end of incubation, no clear effects can be found with exposure to CNTs except for positive effects of 500 μg SWCNTs g^{-1} soil and 1000 μg MWCNTs g^{-1} soil. At the same time, the effects of CNTs on ammonium-oxidizing archaea and ammonium-oxidizing bacteria were observed. The first addition of CNTs had negative effects on abundance of two ammonium-oxidizing microorganisms. Although in the end of incubation, the addition of CNTs had similar results with the control. And repeated exposure of CNTs had positive effects on Shannon-Wiener index (Chen et al., 2015). This suggested that experiments with long incubation time was necessary because the effects of first exposure and repeated exposure may be different. By altering the bacterial community composition, the carbon cycling can be also affected by CNTs. Hao et al, 2018 indicated that the relative abundance of *Proteobacteria* declined with treatment of MWCNTs. At the class level, relative abundance of two dominate bacteria within *Proteobacteria* also decreased. However, the major species remained dominant in community.(Hao et al., 2017). Moreover, Khodakovskaya et al, 2013 found that CNTs resulted in two opposite response of different bacteria. Relative abundance of several bacteria increased while some other bacteria had decreased relative abundance with the treatment of CNTs (Khodakovskaya et al., 2013).This may be correlated with

Table 1
Effects of CNTs on the biodegradation of pollutants.

CNTs	Physicochemical properties of CNTs	Applied dosage	Incubation time	Influence	Biodegradation efficiency	Functional paths	Microbes/ Enzymes	Substrate	Ref
MWCNTs	Outer diameter:10–20 nm Inner diameter:5–10 nm Length:10–30 nm	0, 2,20, and 2000 mg kg^{-1}	90d	No significant effects in low concentration, decreasing degradation in high concentration.	2000 mg•kg^{-1}MWCNTs:26.4%2000 mg•kg-^{1}SWCNTs:25.3%	By reducing activity of microorganisms and decreasing bioavailability of pollutants.	Soil microorganisms	2,4-dichlorophenol	Zhou et al. (2013)
SWCNTs	Outer diameter: < 2 nm Inner diameter:0.8–1.6 nm Length:10–30 nm:5–15 μm	dry soil							
MWCNTs	BET surface area[a]:88 m^2 g^{-1} Meso-pore volume:0.200 cm^3 g^{-1} Micro-pore volume:0.001 cm^3 g^{-1}	mass ratio of MWCNTs to mineral particles was 5:95	28d	Lowering the biodegradation efficiency.	54.2 ± 6.3%	By reducing bioavailability of pollutants.	Agrobacterium	phenanthrene	Xia et al. (2010)
SWCNTs	Outer diameter: 1.2–1.5 nm Length:10–30 nm:2–5 nm	0,0.05,0.1 and 0.5%	80d	Decreasing mineralzation in CNTs-amended soil.	0.5%SWCNTs: 14.4 ± 0.6% 0.5%MWCNTs: 38.3 ± 0.6^9%	By reducing extractability and bioaccessibility. And SWCNTs resulted in lower degradation efficiency.	Soil microorganisms	Phenanthrene, benzo-[a] pyrene	Towell et al. (2011)
MWCNTs	Outer diameter: 10–15 nm Inner diameter:2–6 nm Length:10–30 nm:0.1–10 nm								
SWCNTs	/	/	/	Affecting the biodegradation process.	/	By effects on the interaction of enzyme and substrates.	Manganese peroxidase	Bisphenol A, nonylphenol, triclosan	Chen et al. (2017b)
MWCNTs	Outer diameter:30–50 nm Length: 10–20 μm	0, 25, 50,100 mg kg^{-1}	49d	Decreasing the biodegradation in soil with low organic content. When high concentration of CNTs are added, it increased the biodegradation in soil with high organic content.	Degradation efficiency of phenanthrene in all groups: > 98% Degradation efficiency of pyrene in all groups: > 90%	Decreased degradation due to limited microbial activity, increased degradation by increasing the bioavailability.	Soil microorganisms	Mixture of pyrene and phenanthrene	Shrestha et al. (2015)
MWCNT-1	BET surface area: 159 m^2 g^{-1} Pore volume: 0.870 cm^3 g^{-1} Mean pore diameter:22.0 nm	0, 1.0, 2.5, 5.0, 7.5, 15.0, and 25.0 g	100d	Microbial debromination was inhibited with the application of CNTs. And the larger surface area of carbon nanotubes resulted in the stronger inhibition of debromination.	MWCNT-1:Decreased by 69.2%	By reduced bioavailability of pollutants.	Sediment microorganisms	2,2,4,4-tetrabromodiphenyl ether	Zhu et al. (2016a)
MWCNT-2	BET surface area: 65.9 m^2 g^{-1} Pore volume: 0.247 cm^3 g^{-1} Mean pore diameter:17.1 nm				MWCNT-2:Decreased by 61.6%,				

[a] Means surface areas by nitrogen adsorption using the Brunauer Emmett Teller (BET)method.

the microbial tolerance to CNTs. Some microbes have stronger tolerance and adaptability. Several factors govern the toxicity of CNTs to microorganism would be discussed in next section.

2.2. Microorganisms in wastewater

When dispose municipal and industrial wastewater, activated sludge process is the most commonly used biological process. Activated sludge is the sum total of microorganism population and the organic and inorganic matter they are attached to. Microorganisms in activated sludge play a vital role in degradation and conversion of pollutants (Hai et al., 2014). Since their hydrophobicity, CNTs are easily to aggregate and adsorb to active sludge. The interaction of CNTs and activated sludge can lengthen the retention time of CNTs in sludge. Thus, CNTs have possibility to induce chronic toxicity to microorganisms (Luongo and Zhang, 2010). The toxicity of CNTs to microorganisms may lead to some negative effects on activated sludge process. For example, the treatment efficacy of activated sludge process may be decreased. The possibility of discharging untreated sewage increased. A number of pathogenic microbes and CNTs can find their way into environment (Goyal et al., 2010). In general, effects of CNTs on wastewater treatment process including effects on properties and treatment efficacy of activated sludge, effects on microorganisms. Hai et al. found that the average total nitrogen removal proportion was not clearly affected by 1 mg•$L^{-1}$of MWCNTs. But under 20 mg•$L^{-1}$of MWCNTs, ammonia oxidation declined. The concentration of NH_4^+-N in effluent increased. The average total nitrogen removal efficiency decreased in this condition. Moreover, both of 1 mg L^{-1} and 20 mg L^{-1} of MWCNTs resulted in poor average phosphorus removal efficiency (Hai et al., 2014). CNTs can also have effects on anaerobic digestion process. Anaerobic digestion process including several steps: hydrolysis, acetogenesis, methanogenesis and etc. Suppression of anyone step would lead to the decrease of end product. For example, Yadav et al. observed the decrease of volatile fatty acid (VFA) in all groups treatment with MWCNTs. Accordingly, the production of biogas decreased in different extents with 1or 100 mg•L^{-1}MWCNTs (Yadav et al., 2009). However, there was a contrast result. Li et al. showed a much quickly utilization of substrate and higher removal rate of COD (Chemical Oxygen Demand) with addition of SWCNTs. And the production of CH_4 was much faster. Although the maximum CH_4 volume in reactors exposure to SWCNTs had no significant difference with the control (Li et al., 2015). Several research indicated that CNTs had positive effects on the removal of COD by adsorption in short term. However, long-term exposure to CNTs would result in accumulation of CNTs in sludge. The toxic effects of CNTs to microorganisms increased. Thus, the removal of COD can be inhibited with long-term exposure to CNTs (Hai et al., 2014).The conductivity of sludge can be altered by SWCNTs. Activated sludge had less negative charge with exposure to SWCNTs (Yin and Zhang, 2008).And it was suggested that the settleability of sludge improved by CNTs. On the one hand, the interaction between CNTs and sludge made density of flocs be increased. On the other hand, the relative abundance of microbes related to the flocculation of activated sludge increased (Qu et al., 2015). The relative abundance of microbes responsible for sludge bulking decreased (Hai et al., 2014). In fact, CNTs may affect the treatment efficacy of wastewater treatment system by impacts on microbes. Qu et al. showed that relative abundance of *Rudaea* increased with exposure to SWCNTs. *Rudaea* was regarded as potential degradation bacteria for aromatics and can degrade cellulose. Therefore, SWCNTs may improve the degradation of aromatic. In fact, the study suggested that the removal of phenol increased after addition of SWCNTs especially in the early stage (Qu et al., 2015). Yadav et al. observed that decrease of production of biogas was due to damage of acidogenic and acetogenic microbes by MWCNTs (Yadav et al., 2009). In summary, the positive or negative effects of CNTs on activated sludge process seemingly related to impacts on microorganism population.

2.3. Microorganisms in other conditions

The interaction between CNTs and microorganisms in culture medium is not complicated like in natural environment. Qu et al. found that with nothing act as carbon source, the death rate of *Dyella ginsengisoli* LA-4 was related to the concentration of CNTs in aqueous medium. When biphenyl served as carbon source, each of 1.5 mg L^{-1} SWCNTs, 1.5 mg L^{-1} SWCNTs-COOH and 1 mg L^{-1} MWCNTs stimulated the growth of *Dyella ginsengisoli* LA-4. However, this kind of stimulation function was not reflected in the degradation of biphenyl (Qu et al., 2016). It might indicate that CNTs enhance or inhibit biodegradation by balancing two effects: the toxicity of CNTs to microorganisms and effects on bioavailability of pollutants (Zhang et al., 2015).

Some carbonaceous materials including CNTs are often used as sorbents for sediment remediation. These sediments may be contaminated by organic pollutants, and heavy metals. In this environment consist of CNTs, pollutants and microbes, the interaction between them would be critical for remediation. In a fresh water sediment contaminated by crude oil, the total abundance of microbes was increased by amendment with 0.1% CNTs. 0.5% and 1% CNTs increased the abundance of microbes in higher concentration of crude oil. It may be due to that CNTs can adsorb hydrocarbons and microbes simultaneously. And CNTs served as microenvironments to accelerate the growth of microbes. Not only the toxicity of hydrocarbons decreased, but also the utilization of hydrocarbons by microbes was promoted (Abbasian et al., 2016). The effects of CNTs on properties of microbes in different environment are listed in Table 2.

2.4. The toxicity mechanism of CNTs against microorganisms

Cell viability and metabolic function of microorganisms which play a key role in the biodegradation of contaminants are often influenced by CNTs. It is generally resulted from the toxicity of CNTs to microbes (Liu et al., 2019). Over recent decades, a majority of papers about the toxicity of CNTs have been published and various toxicity mechanisms have been explored. However, the toxicity mechanisms in the current studies are scarce and usually inconsistent. In the following section, some toxicity mechanisms of CNTs to microorganisms will be discussed in detail.

The proposed toxicity mechanisms of CNTs are as follows: interrupting transmembrane electron transfer, disrupting/penetrating the cell membrane and oxidating cell components etc. Besides, the eukaryotic cells have other specific toxic mechanisms such as mitochondrial dysfunction. Direct contact between CNT aggregates and cells was observed by fluorescence-based images which could be the primary cause of cell inactivation (Kang et al., 2007). Bacteria cells lost their cellular integrity and the cell membrane was damaged after exposure to CNTs (Kang et al., 2007). Cell membrane damage caused by physical puncture was believed to be the main cause of the cell death other than inhibiting cell growth or oxidative stress (Liu et al., 2009). However, another study showed that in two kinds of CNTs: SWCNTs and MWCNTs, only the former exhibited antimicrobial activity while the other did not exhibit such activity. Hence, in addition to the toxic mechanism of direct contacts between cells and CNTs, the researchers proposed that there might be other factors concerned to the antimicrobial activity (Arias and Yang, 2009).

Residual catalysts from the preparation of CNTs probably generate hydroxyl radicals, which can reduce the cell viability and promote the intracellular reactive oxidative species (ROS) (Chang et al., 2014; Esimbekova et al., 2017; Visalli et al., 2017). However, extensively studies have shown that CNTs can be highly purified and remove impurities (Zhu et al., 2016b). Therefore, residual catalysts may not be the crucial reason of the toxicity of CNTs. As for ROS, they were considered to be associated with oxidative damage. Metal nanomaterials and the released components such as metal impurities and amorphous carbon

Table2
The effects of CNTs on microorganisms.

Environment matrix	CNTs	Physicochemical properties of CNTs	Applied dosage	Toxic effects	Ref
Soil	SWCNTs	Outer diameter: < 2 nm	100, 200, 500 μg g^{-1} soil	SWNTs first decreased the biomass carbon and the highest concentration of SWNTs produced a significant positive effect on biomass carbon; Negative effects on the abundance of ammonium oxidizing microbes; Some species disappeared while some species emerged.	Chen et al. (2015)
	MWCNTs			Reduction on biomass carbon with the increasing concentrations of MWNTs. Negative effects on abundance. Modification of community structure after the experiment.	
	MWCNTs	Length:10–20 μm Diameter:15.1 ± 1.2 nm	50, 500, 5000 mg g^{-1} soil	Decrease of soil microbial biomass at the high MWCNTs concentration.	Chung et al. (2011)
	SWCNTs	Average length:1.02 μm Average diameter: 1.0 nm	0,30,100,300,600,1000 μg g^{-1} soil	Biomass C and N decreased with higher concentration of SWCNTs. Larger effect of powder form SWCNTs than suspended form SWCNTs.	Jin et al. (2013)
	SWCNTs	Average length:1.02 μm Average diameter: 1.0 nm	0.03,0.1,0.3,0.6, 1 mg g^{-1} soil	Negative relationship between SWCNTs concentration and biomass. The relative abundance of total bacteria was positively related with SWCNT concentration. Changes in microbial community composition can be found.	Jin et al. (2014)
	MWCNTs	Inner diameter:10 nm Outer diameter:25 nm	50,200 μg•mL−1	No negative effect of MWCNTs on bacterial diversity, but a significant modification of the bacterial community composition was observed. Decreased relative abundance on some genera like Proteobacteria and Verrucomicorbia and increased abundance of Bacteroidetes and Firmicutes.	Khodakovskaya et al. (2013)
Aqueous medium	SWCNTs MWCNTs SWCNT-COOHs	Length: 5–15 μm Diameter: < 2 nm Length: 5–15 μm Diameter: < 10 nm Length: 30 μm Diameter: < 2 nm	0.5,1,1.5,2,5,10,20 mg L^{-1} 0.5,1,1.5,2,5,10,20 mg L^{-1} 0.5,1,1.5,2,5,10,20 mg L^{-1}	Bacterial cell viability loss. Toxicity was as follows: MWCNTs > SWCNT-COOHs > SWCNTs.	Qu et al. (2016)
	MWNTs	Length: 1.0–2.0 μm Diameter: 10–20 nm	5,25,100 mg•L-1	No effects of 25 mg/L CNTs on bacterial growth. Reduction on biomass with 25 mg/L or 100 mg/L CNTs.	Zhang et al. (2015)

(*continued on next page*)

Table2 (*continued*)

Environment matrix	CNTs	Physicochemical properties of CNTs	Applied dosage	Toxic effects	Ref
Activated sludge	SWCNTs	Average outside diameter:1–2 nm Length:5–15 μm	219 mg L^{-1}	SWCNTs changed microbial community structure in activated sludge batch reactors through toxicity to some community members.	Goyal et al. (2010)

can generate radicals, which belong to ROS (Chang et al., 2014). Both of the formation of radicals such as superoxide radical anions and hydroxyl radicals and the activation of oxidative ROS-related enzymes and receptors can lead to oxidative stress; (Chang et al., 2014; Shvedova et al., 2012). Exceeding oxidative stress not only increase the concentration of cytosolic calcium and change the location of transcription factors (e.g. NF–B) to the nucleus, but also stimulate the oxidation of the double bonds on fatty acids of phospholipids in the cell membrane. The peroxidized fatty acids can further produce free radicals, subsequently oxidized subcellular components which can result in cell necrosis or apoptosis in different degrees. In fact, the cells have a defense mechanism that can resist the reactive oxygen species. The defense mechanism will be detailed in the following sections. Quantities of ROS induced exceeding oxidative stress that may result in an imbalance between oxidation and anti-oxidation processes. As a result, the cell is dead due to exposing to CNTs. The activation of ROS-related enzymes and receptors is another way to induce oxidative stress. It can also produce radicals by changing the function of protein and chemical fragmentation (Riding et al., 2011).

As proved by Zhu et al.2016a,b, mitochondrial impairment might also result in apoptosis (Zhu et al., 2016b). The apoptosis can be induced by some morphological changes of mitochondria, such as mitochondrial fusion and cristae remodeling. Moreover, the release of cytochrome from mitochondria and the reduction in mitochondrial transmembrane potential (MTP) are two symbols of apoptotic process (Zhu et al., 2016b). In addition, Chang et al. proposed an unusual nanotoxicological mechanism about depleting nutrients (Chang et al., 2014). It was found that CNTs could deplete amino acids and vitamins from cell culture medium. And CNTs induced toxicity via this pathway could be mitigated by supplying additional folate (Klaine et al.2008).

Throughout the above, the toxicity mechanism of CNTs to microorganisms was the joint effect of physical and chemical action. Many toxicity mechanisms might play a role simultaneously or act in succession. Synergy and antagonism could also occur (Pasquini et al., 2013). All sorts of reasons make it more complicated to determine the true toxicity mechanism of CNTs. To better understand the existing researches on the toxicity mechanism of CNTs, the schematic representation of the toxicity mechanism was shown in Fig. 2 (take eukaryocyte as an example).

2.5. The protection and adaption mechanism of microorganisms to CNTs

Although CNTs may be toxic to microbes by the above mechanisms, microbes which exposed to CNTs also have their own protection and adaptation mechanisms. And the protection and adaptation mechanisms are shown in Fig. 3. The high-molecular weight compounds called as EPS (extracellular polymeric substance) which from natural secretions of microorganisms cells, cell lysis, hydrolysis productions of wastewater and etc.(Luongo and Zhang, 2010). When cells exposed to CNTs, EPS can be attached to surface of cells and act as protective shield to prevent CNTs from penetrating cells or resist ROS(Li et al., 2015; Rodrigues and Elimelech, 2010; Shao et al., 2017). Besides, CNTs can destabilized and penetrate into bacterial membrane. It is an important mechanism resulted in the inactivation of bacteria. However, there is an effective adaption mechanism which can increase the tolerance of bacteria to CNTs. *Escherichia coli* and one kinds of polybrominated diphenyl ether degrading strain called as *Ochrobactrum* sp., showed the increased level of saturated fatty acids and the reduced level of unsaturated fatty acids after treated with 50 mg L^{-1} CNTs. The fatty acid profiles of *Staphyloccocus aureus* and *Bacillus subtilis* are composed of branched-chain fatty acids and saturated straight chain fatty acids. By the treatment of 50 mg L^{-1} CNTs, the proportion of straight chain fatty acids was reduced and branched-chain fatty acids increased. Through such an adaptation mechanism by changing the composition of fatty acid, the physical structure of membrane are maintained. The interaction degree between CNTs and cells are reduced. Therefore, the function of bacterial membrane which including controlling the movement of substances into or out of cells and maintaining homeostasis was remained. (Zhu et al., 2014).

2.6. Factors affecting the role of CNTs on microbial biodegradation

The results of CNTs toxicity tests in previous studies were often not quite the same. One explanation of this difference is that the cytotoxic effects of CNTs on microbes are not a function of a single mechanism, but rather depend on a majority of factors (Kang et al., 2008b; Simon et al., 2014).The physicochemical properties of CNTs, as well as the organism itself and the medium environment may have varying degrees of influence. Several factors were studied and discussed below (Table 3).

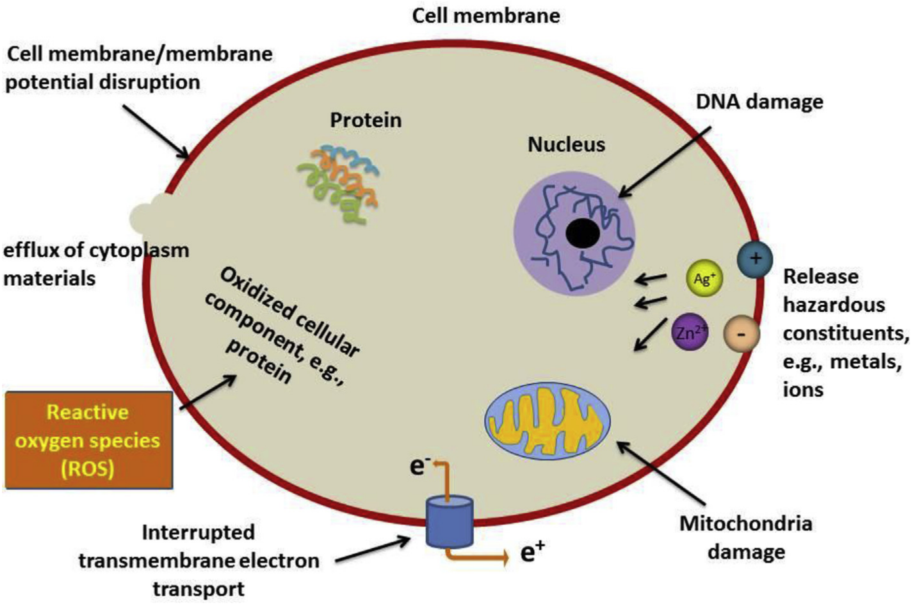

Fig. 2. Different toxicity mechanisms to eukaryotic cells of CNTs.

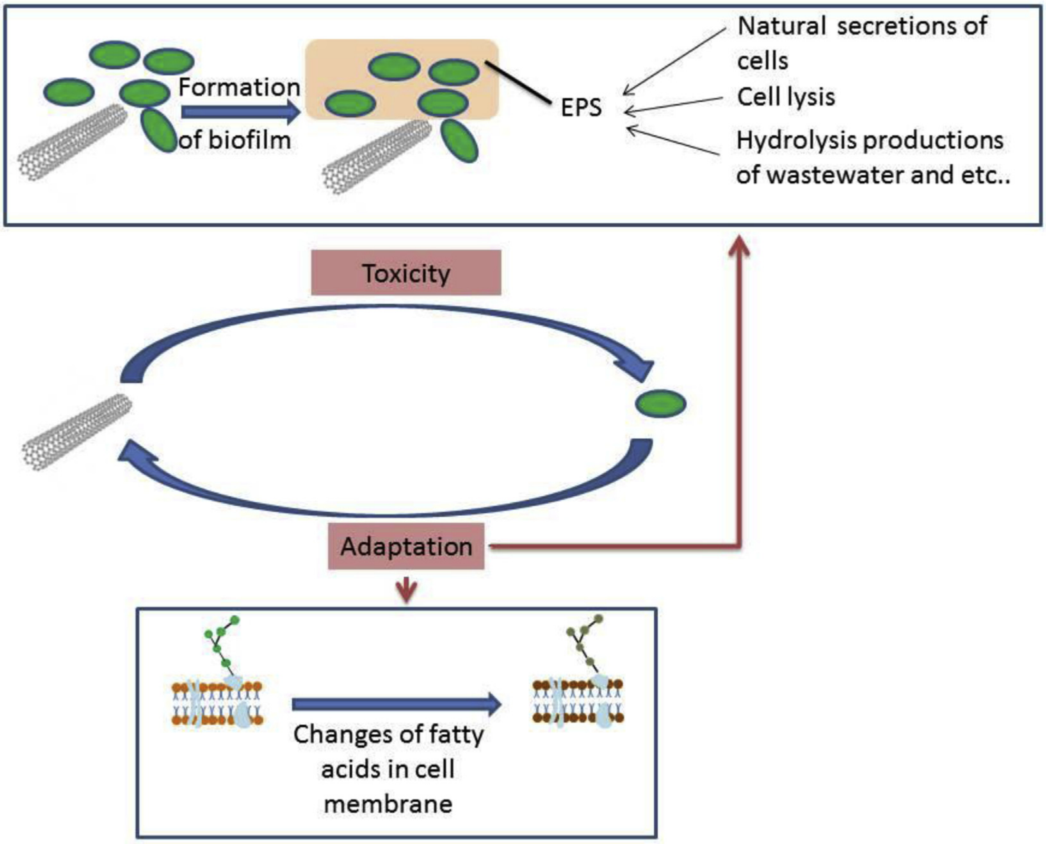

Fig. 3. The protection and adaption mechanisms of microorganisms to CNTs.

2.7. Physicochemical properties of CNTs

When conducting toxicity test, the size of CNTs is a factor that cannot be ignored and plays an important role in the damage of bacteria cells. It was well documented that the interaction of CNTs with living cells exhibited a size-dependency (Kang et al., 2008a; Shrestha et al., 2013). At the same concentration, the reduction of bacterial viability by $MWNT_{40\text{-}60}$ (diameter of 40–60 nm) was more serious than that of $MWNT_{60\text{-}100}$ (diameter of 60–100 nm), which demonstrated the stronger cellular toxicity of smaller-diameter MWCNTs (Yang et al., 2017). Bai et al. (Bai et al., 2011). found that SWCNTs could not only capture cells but also effectively killed cells through physical puncture. However, MWCNTs had only the same effect as SWCNTs on the capture of cells. The reason might be that MWCNTs had larger diameter than

Table 3
Determinants of CNTs toxicity.

Factors type	Impact factors	Effects on CNTs toxicity	References
CNTs	Diameter	SWCNTs with smaller diameter exhibited stronger antimicrobial activity than larger-diameter SWCNTs and MWCNTs	Klaine et al. (2008)
	Length	Different lengths of SWCNTs (1, 1–5, and ~5 μm)at same weight concentrations, the higher-length SWCNTs have stronger toxicity	Yang et al. (2010)
	Surface area	SWCNTs had larger specific surface area leading to stronger toxicity than MWCNTs.	Kang et al. (2008a)
	Concentration	A dose-dependency effect on soil microbial activity was observed with SWCNTs. The higher concentration of SWCNTs, the greater impact on microbial community.	Rodrigues et al. (2013)
	Electronic structure	The toxicity of three different electronically metallic (> 95%M), semiconducting (< 5%M), and mixed (~30%M) SWCNTs were investigated. Both SWNT toxicity assay (suspended toxicity assay and filter toxicity assay) showed that the metallic nanotubes had the strongest toxicity.	Vecitis et al. (2010)
	Surface defects	The adhesion of MWCNTs on the cell membrane was influenced by the extent of surface defects including incomplete bonds, surface functionalities, sp^3 hybridized carbon atoms and ring shapes other than hexagon	(Jiang et al., 2017) (Charlier, 2002)
	Dispersion/aggregation state	Better dispersion of functionalized MWCNTs increased the interaction with cells and therefore increased the toxicity.	Zhou et al. (2017)
Environmental condition	Natural organic matter	Due to the existence of humic acid, the toxicity effects of both as-grown MWCNTs (A-MWCNTs) and HNO_3-treated A-MWCNTs (H-MWCNTs) were reduced.	Chi et al. (2016)
	Solution type	When using different media, (deionized water, NaCl, PBS buffer, and brain-heart infusion broth) SWCNTs exhibited highest antimicrobial activity in the deionized water and NaCl, no antimicrobial activities can be observed in PBS buffer and brain-heart infusion broth.	Bradyestévez et al. (2010)
Others	Bacterial type	The toxicity of MWCNTs on gram-positive bacteria (B. *subtilis*) was stronger than that of gram-negative bacteria (E. *coli*) with an outer membrane.	Yang et al. (2017)
	Incubation time	The antimicrobial activity increased with the increase of time.	Amiri et al. (2016b)

SWCNTs. The similar conclusions were also found in other researches (Amiri et al., 2016; Jia et al, 2005 Yang and Xing).

Compared with the size (diameter), there are few reports about the effect of length on the toxicity of CNTs. Even though, the length of CNTs also matters. The results of studies on the effects of length are clearly divided into two opposed groups. One thought that short SWCNTs were more toxic to microorganisms (Klaine et al.2008), and the other supported that longer SWCNTs exhibited stronger toxicity (Yang et al., 2010). It was observed that shorter SWCNTs were prone to self-aggregate, while longer SWCNTs tended to form aggregations with lots of bacterial cells (Yang et al., 2010). Zhu et al. indicated that it was helpful for long SWCNTs with the highest absolute electrophoretic mobility to contact with bacteria. Because longer SWCNTs had better dispersion and stability. (Zhu et al., 2014). However, the long CNTs did not always display higher toxicity than short CNTs. This shows that although the length is related to the toxicity of CNTs, it is not the determining factor in cytotoxicity (Kang et al., 2008b).

Several studies have shown that the toxicity of SWCNTs is different from that of MWCNTs. To be exact, SWCNTs are more toxic than MWCNTs (Qu et al., 2016; Yang et al., 2017). It is well known that the surface area of CNTs is an important characteristic from a toxicological perspective (Kang et al., 2008a). Jin et al. suggested that, although the concentration was approximately 5 times lower, SWCNTs showed similar toxic effects to MWCNTs (Jin et al., 2013). This was owing to the same concentration of CNTs, SWCNTs have a higher specific surface area than the multi-walled one. Kang et al. found that most of the *E. coli* cells lost their cell activity and cellular integrity when exposed to SWCNTs. Conversely, MWCNTs had only a slight effect on cellular integrity (Kang et al., 2008a). The stronger toxicity of SWCNTs might be due to the smaller diameter and the larger surface area than MWCNTs.

The concentration/dose of CNTs applied to study is also a critical factor for antimicrobial activity of nanostructures. In general way, when the dosage of CNTs increased, the level of cytotoxicity increased correspondingly. In addition, no significant toxicity can be observed for CNTs up to a certain value (Amiri et al., 2016b). Increasing the applied dose of CNTs would like to increase the surface area of CNTs, some adverse effects on microorganisms were enhanced. The similarity between the samples treated with different concentration of CNTs could indicate the changes of bacterial community. The control and the CNTs-20 group (20 μg mL^{-1} of CNTs) had higher similarity than the CNTs-50 group and CNTs-200 group, which showed higher effects on microbial community of high exposure level. Other studies also confirmed low concentration of CNTs having no significant or minor effects on microorganisms while high concentration of CNTs having greater impacts on microorganisms (Hao et al., 2018; Khodakovskaya et al, 2013; Rodrigues et al.2013; Zhu et al., 2016b). It is noteworthy that some papers have shown that low concentration of CNTs can improve the growth of microbes including functional bacteria and biofilm formation in some cases which proved by previous section (Rodrigues and Elimelech, 2010; Simonin and Richaume, 2015). Interestingly, this kind of concentration-dependency was also reflected in the mineralization of pollutants (Zhang et al., 2015; Zhou et al., 2013). Zhu et al. confirmed that the reciprocal of BDE-47 (2,2,4,4-tetrabromodiphenyl ether) debromination ratio (1/R) was proportional to the concentration of carbonaceous materials (black carbon, CNTs) amended in sediments. And the reciprocal of the concentration of lower brominated congeners (1/C) also increased with increased concentration of carbonaceous materials.(Zhu et al., 2016a). Therefore, in order to mitigate adverse environmental effects, it is necessary to determine the minimum concentration of CNTs exhibiting toxicity.

Pristine CNTs without any hanging bonds make them chemically inert and incompatible with nearly all solvents. The wide application of CNTs is limited (Lanone et al., 2013). Therefore, the surface functionalization which attaches different functional groups to CNTs is used to improve their solubility and dispersion, allowing versatile applications (Su et al., 2015; Zhou et al., 2017). At the same time, however, the toxicity of CNTs is also changed. There are two inconsistent tendencies when CNTs are modified by surface functionalization. On the one hand, the functionalization of CNTs may enhance the toxicity. At 200 μg mL^{-1}, CNTs-OH and CNTs-COOH(CNTs functionalized with hydroxyl functional group, carboxyl functional group) resulted in significant membrane damage while no significant membrane damage can be found in which exposed to pristine form CNTs (Zhou et al., 2017). The antifungal activity of MWCNTs-lysine and MWCNTs-arginine against various funguses was multiplied up many times compared to that of pristine MWCNTs (Zare-Zardini et al., 2013). Increased toxicity might be due to the enhanced CNT hydrophilicity, the increased opportunity internalized by cells, and the change of surface charge (Jiang et al., 2017; Zare-Zardini et al., 2013). On the other hand, with the degree of sidewall functionalization enhanced, the toxicity of SWCNTs decreased (Sayes et al., 2006). In a work of Chen and co-workers, the functionalized CNTs were found to be nontoxic. However, unmodified CNTs induced cell death (Chen et al., 2006). Chi et al. (2016) found in both of medium A and medium B (trace elements and vitamins of glucose minimal salt were replaced by 0.25 g L^{-1} or 0.025 g L^{-1} yeast extract), the antibacterial activity of A-MWCNTs (as-grown MWCNTs) was more significant than H-MWCNTs (HNO_3-treated A-MWCNTs). It was observed by the loss of viability. Stronger electrostatic repulsion effect may be responsible for the less loss of viability with H-MWCNTs. Interestingly, Pasquini et al. (2012) investigated nine functionalized SWNTs (fSWNTs). Compared with the pristine SWCNTs, the percent cell viability loss caused by these nine fSWNTs was either increased or decreased, or similar to that of starting material. These nine functionalized SWCNTs had different functional groups, which made them have varying physicochemical properties such as molecular size, surface charge, element composition etc.. Therefore, it seems plausible that adding different functional groups had different impacts on the toxicity of CNTs. And it was claimed that the toxicity of SWCNTs can be indirectly changed by functionalization with covalent surface functional groups and mechanical stirring. The indirect effect is derived from the degree of dispersion (Pasquini et al., 2012).

Direct contact with bacteria by CNTs is an important mechanism contributing to CNTs bacterial cytotoxicity. Therefore, increasing cell exposure by controlling the physicochemical properties of CNTs may be one of the way to increase bacterial cytotoxicity (Kang et al., 2008b; Pasquini et al., 2013). The factors such as the exposed CNTs surface area, aggregation behavior, and solution chemistry can mediate the extent of bacterial-CNTs contact (Vecitis et al., 2010). In general, the highly dispersed CNTs have more accessible surface area. So it is helpful for CNTs to contact with bacterial cells, increased interactions and high toxicity to bacterial cells should be observed (Chi et al., 2016; Zhou et al., 2017) Similarly, Kang et al. observed that uncapped, short and dispersed nanotubes showed high toxicity(Kang et al., 2008b). However, pristine MWCNTs at 200 μg ml^{-1} with addition of BSA (0.5% bovine serum albumin) did not increase cell viability. The result might be due to that the so dispersed MWCNTs cannot be further dispersed by additional BSA. The agglomeration state of CNTs can mediate their size distribution, available specific area, and their surface reactivity which relevant to the toxicity of nanoparticles. Now, diverse types of methods (sonication, detergents, surfactants, polyethylene glycol, serum, etc.) can be used to deagglomerate nanoparticles (Bai et al., 2011; Dhawan and Sharma, 2010). Bai et al. (2011) used three different surfactants to disperse MWCNTs and examined the antibacterial activity of aqueous dispersion. The results suggested that the toxicity of MWCNTs dispersed by CTAB (hexadecyltrimethylammonium bromide) was stronger than that of MWCNTs dispersed by SDS (sodium dodecyl sulfate) and TX-100 (Triton X-100). That might be due to the antibacterial activities of surfactants themselves, and CTAB solution had the strongest antibacterial (Liu et al., 2012a).

2.8. Effects of microbes

It was speculated that both of the physicochemical properties of CNTs and bacteria corresponding to the viability of bacteria in the presence of CNTs (Zhu et al., 2014). The membrane structure of gram-positive bacteria and gram-negative bacteria is different. The gram-negative bacteria have an outer membrane composed of the porin and lipopolysaccharide molecules, and the gram-positive bacteria have no such outer membrane. Yang et al. suggested that the inactivation of gram-positive *B. subtilis* was stronger than that of gram-negative *E. coli* (Yang et al., 2017). However, bacterial inactivation does not always follow this pattern. Arias and Yang found the differences in the structure and shape of gram-positive bacteria and gram-negative bacteria not affecting the antimicrobial efficacy of SWCNTs. Moreover, the charge effect between the SWCNTs and the cell walls surface might not play vital roles in controlling the toxicity of SWNTs to cells (Arias and Yang, 2009; Liu et al., 2011). Though electrostatic repulsion at the interface between the MWCNTs and the bacteria could partially reduce toxicity. In addition, microbial tolerance toward CNTs could also lead to different reactions to the antimicrobial activity of CNTs. As demonstrated by some researchers, *Trabusiella guamensis* could adapt and tolerate carbon nanomaterials. Thus, the bacteria could survive in a goldsmith site contaminated with nanomaterials. Moreover, *Trabusiella guamensis* was observed transforming MWCNTs through the oxidation process (Chouhan et al., 2016).

2.9. The role of environment matrix

In the natural environment, the toxicity of CNTs are closely related to environmental parameters, including solution type, pH and organic matter content (Lawrence et al., 2016b, 2016c). Researchers investigated the antimicrobial activity of SWCNTs with different surface groups (SWNTs-OH, SWNTs-COOH and SWNTs-NH_2) to bacteria in different buffers (DI water, 0.9% NaCl, 0.1M PBS, and BHI broth). In the presence of 100 μg mL^{-1} SWNTs-OH and SWNTs-COOH, *Salmonella* cells incubated with DI water delayed their growth time for about 1.5 h, while at the same concentration of SWNTs-NH_2, cells in DI water grew at a similar rate as the control sample. As a contrast, when the buffer was replaced by 0.9% NaCl, *Salmonella* cells treated with SWNTs-OH and SWNTs-COOH showed no growth in 7 h, while the control sample and the cells treated with SWNTs-NH_2 started grow 4 h earlier. Moreover, SWNTs-OH and SWNTs-COOH exhibited extremely strong antimicrobial activity to both gram-positive and gram-negative bacterial cells in DI water and 0.9% NaCl solution regardless of cell shape, but no antimicrobial activity could be observed in PBS buffer and brain heart infusion broth. It was noteworthy that the pH of these four buffers was approximately the same, whereas these buffers had different ionic strengths. Therefore, the pH did not work here. The ionic strengths might account for different results (Arias and Yang, 2009). Interestingly, in an experiment with four CNTs which had different metal species and metal contents, the pH dependence of the radical generation was observed by ESR (Electron spin resonance) spectroscopy in conjunction with a spin-trapping technique. The results suggested that lower pH resulted in stronger ESR signal. Very weak signals could be observed in a neutral environment. This kind of pH dependence might be interpreted by the low solubility of metal ions and poor leaching of metals from CNTs at high pH (Ge et al., 2012).

Apart from that, natural organic matter (NOM) as ubiquitous component of aquatic systems or soil might have a protective effect. These organic matter compounds might be adsorbed to the surfaces of CNTs and thus affect their surface speciation and charge (Amiri et al., 2016b). Furthermore, NOM could exert electrostatic hindrance to minimize direct contact between CNTs and bacteria. Then, the toxicity decreased (Chen et al., 2011a). When CNTs were added to two different soil, the basal respiration which reflects intrinsic soil microbial activities was typically much higher in Drummer soil with higher organic content than in Tracy soil (Tong et al., 2012). The coating of humic acid (HA) could mitigate the toxicity of MWCNTs by increasing steric and electrostatic repulsive forces (Chi et al., 2016). Lawrence et al. similarly reported that CNTs coating with biomacromolecules such as protein and polysaccharide had lower toxicity. These biomacromolecules reduced the production of ROS and thus resulted in a reduction of CNTs toxicity to bacteria (Lawrence et al., 2016a).

2.10. Other factors

Except for the factors mentioned above, there are many other factors that work in the antimicrobial activity of CNTs. On the one hand, prolonged exposure time might increase the toxicity of CNTs (Kang et al., 2009). On the other hand, the toxic effects of the first exposure to CNTs would disappear when the contact period increased (Shrestha et al., 2013). Anyhow, there is no doubt that various factors such as properties of CNTs and microbes, ambient environment and operating conditions might affect the antimicrobial activity of CNTs. Therefore, before the toxicity test of CNTs, it is crucial to purify and characterize them (Liu et al., 2009). More extensive characterization should include the descriptions of physicochemical properties such as size, shape, solubility, agglomeration, elemental purity, surface area and so on, while incomplete characterization can lead to the difficult in comparison with other research results. And it can further lead to the failure to draw a definitive conclusion about the effect of a factor on the antimicrobial activity (Dhawan and Sharma, 2010).

2.11. Effects of CNTs on the activity of enzymes

Microbial functions are closely associated with their enzymes. Degradation of pollutants, reproduction, development, nutrient uptake and growth require the participation of various enzymes. For instance, LiP (lignin peroxidase) is one of the ligninolytic enzyme which can metabolize several pollutants (Chen et al., 2017b). Many microbes are able to secrete this kind of enzyme (Asgher et al., 2012). However, it was found that biodegradation activity might be influenced by the interaction between CNTs and degradation enzymes (Liu et al., 2018a, 2018c; Zhang et al., 2015). It was found that with the treatment of SWCNTs or MWCNTs, the activity of catalase directly relevant to the degradation of perhydrol was stimulated in the first three days. However, there was a decrease of catalase activity from the seventh day and kept stable on the fourteenth day compared to those under control (He et al., 2015). The SWCNTs-OH inhibited the utilization of gloucse and the activities of three kinases (i.e., hexokinase (HK), 6-phosphofructose kinase (PFK), and pyruvate kinase (PK)) which played essential roles in glycolysis process. By the inhibition towards nitrate reeducate (NAR), the reduction of nitrate was hindered by the SWCNTs-OH amendment (Su et al., 2015). However, CNTs did not always show adverse effects on enzymes. Jin et al. depicted that 1000 mg g^{-1} soil of SWCNTs in powder form can reduce the activities of most soil enzymes whereas the activity of L-leucine aminopeptidase was increased compared to the control (Jin et al., 2013). Hai et al. (2014) confirmed that two key enzymes participating in the process of nitrification were significantly repressed by long-time exposure to 20 mg L^{-1} MWCNTs. The activity of two enzymes were also decreased which relevant to phosphorus removal. On the other hand, no influence of long-time exposure to 1 or 20 mg L^{-1} MWCNTs on the activity of NAR and nitrite reductase (NIR) can be observed. Furthermore, Ren et al. (Qu et al., 2016; Ren et al., 2012) revealed that the activity of horseradish peroxidase (HRP) in oxidizing the reducing substrates could be enhanced in the presence of unmodified and carboxylated SWCNTs. This positive effect might be associated with increased enzymatic oxidation activity to substrate. In fact, similar to the effects on microorganisms, the different effects of CNTs on enzymes are not only related to the type of enzyme, but also to the type and concentration of CNTs. In addition, CNTs can disturb the enzymatic catalytic oxidation to substrate by different mechanisms

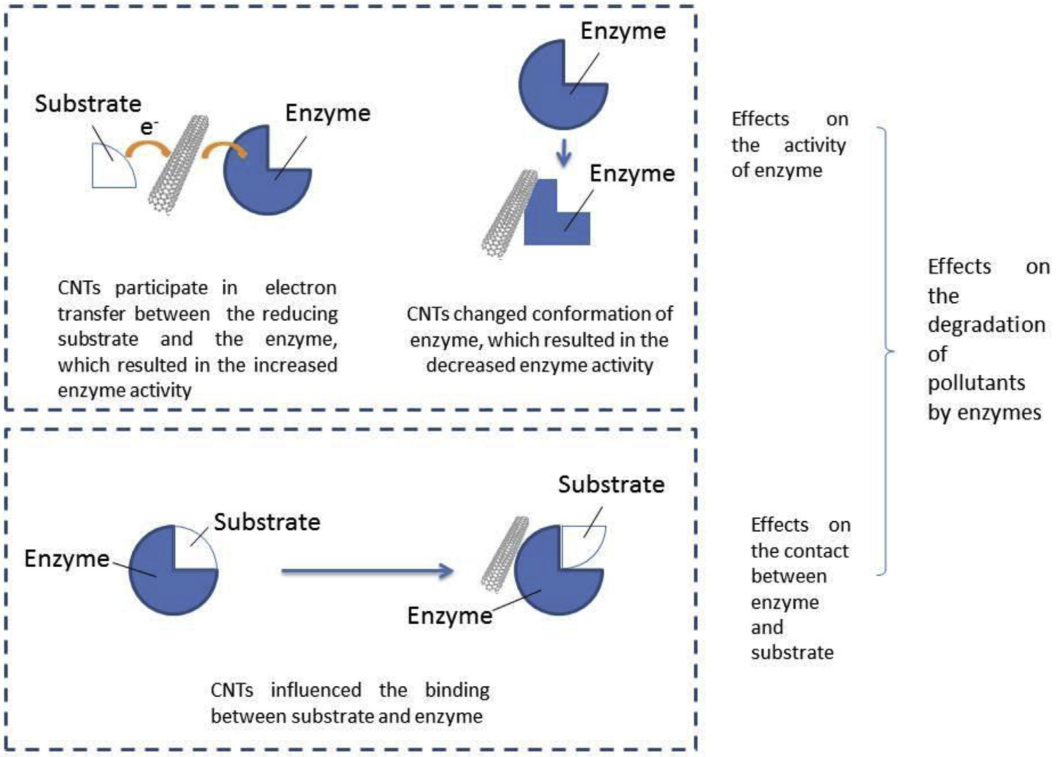

Fig. 4. Mechanisms of CNTs affecting the biodegradation by enzyme.

(Fig. 4). One is related to the inaction of enzymes by changing enzymatic conformations (Liu et al., 2012b). There were some papers that showed other mechanisms. For instance, there were four functionalized MWNTs that site-specifically bind to the catalytic site of α-chymotrypsin (ChT) and competitively inhibited enzymatic function (Zhang et al., 2009). Some previous studies proposed that the barrier effect of polyesters degraded by enzyme mainly due to the lower available surface caused by nanofillers (Bikiaris, 2013). Similarly, SWCNTs influenced the binding stability and binding affinity between corresponding enzymes and their substrates. It was due to the changes of binding energy, water molecular behavior and interaction between enzyme and substrate. Therefore, the microbial enzyme-catalyzed oxidation processes was influenced (Chen et al., 2016). Furthermore, Chen et al. (Ming et al., 2017) indicated that graphene (GRA), SWCNT or SWCNT + GRA had a tendency to decrease the overall bind stability between manganese peroxidase (MnP) and its substrates though the SWCNTs had little impact on the binding energy.

Overall, assessing soil enzyme activities can not only provide information about changes in soil organic matter dynamics but also figure out the nutrient cycling in the presence of contaminants such as CNTs (Shrestha et al., 2013). It must be pointed out that special degradation enzymes could only be produced by certain microorganisms, therefore, the changes in enzyme activity could reflect changes in the activity of certain microbial communities. In other words, CNTs might affect the active microorganisms, thus affecting the activity of enzymes (Jin et al., 2013).

2.12. *Effects of CNTs on contaminants bioavailability*

Except for impacts on microorganisms and enzymes, CNTs can affect the biodegradation of pollutants by effects on bioavailability. In fact, a research found that it was not the inhibition of microbial activity but rather limited bioavailability of contaminants reducing the biodegradation (Xia et al., 2010; Zhou et al., 2013). Xia et al. (2013) found that the density of bacteria showed a significant positive relationship with the mineralization efficiencies after incubation for 35 d. However, there was no significant increase of mineralization efficiencies after the addition of 5 ml cell suspension containing approximately 10^8 cells. Therefore, Xia et al. concluded that limited biodegradation might be due to the reduced phenanthrene which can be available to degrader (Xia et al., 2013). Marchal et al. similarly showed that low mineralization rate was resulted from limited PAHs that can be available. And inhibition of bacterial activity was not the primary reason (Marchal et al., 2013). As CNTs have highly hydrophobic surface, they exhibit strong sorption affinity for a wide range of organic compounds such as HOCs and PAHs(Chen et al., 2011b; Linard et al., 2015a; Zhang et al., 2016).It is clearly that the introduction of CNTs into environment would alter the transport, bioaccumulation, toxicity and bioavailability of pollutants (Kah et al., 2017; Li et al., 2013a). Bioavailable organic compounds were the compound having the potential to access to organisms or the fraction which could desorb from solids to the aqueous phase at equilibrium (Lydy et al., 2015). Through the adsorption on CNTs, the organic pollutants in aqueous phases as well as the fraction in the rapidly desorbing can be reduced. The bioavailability of organic compounds is reduced, correspondingly (Ren et al., 2018a; Semple et al., 2007). When MWCNTs addition with fluoranthene, the response of *Pimephales promelas* was different from those groups without MWCNTs. Around 60%–90% of fluoranthene was adsorbed on MWCNTs. It indicated that MWCNTs reduced the bioavailability of fluoranthene by adsorption (Linard et al., 2015b).Cui et al. showed that both of SWCNTs and black carbon reduced the bioavailability of phenanthrene in sediment. And the mineralization of phenanthrene was inhibited due to reduced freely dissolved concentration of phenanthrene (Cui et al., 2011).Xia et al. similarly found that MWCNTs had negative effects on the bioavailability of phenanthrene to Agrobacterium (Xia et al., 2010).However, Vithanage et al. examined the remediation effects of CNTs and biochar on shooting range soils. They found that CNTs and biochar were effective in immobilizing Pb and Cu, but both of them increased the bioavailability of Sb(Vithanage et al., 2017).Generally, microorganisms can only utilize the compound that

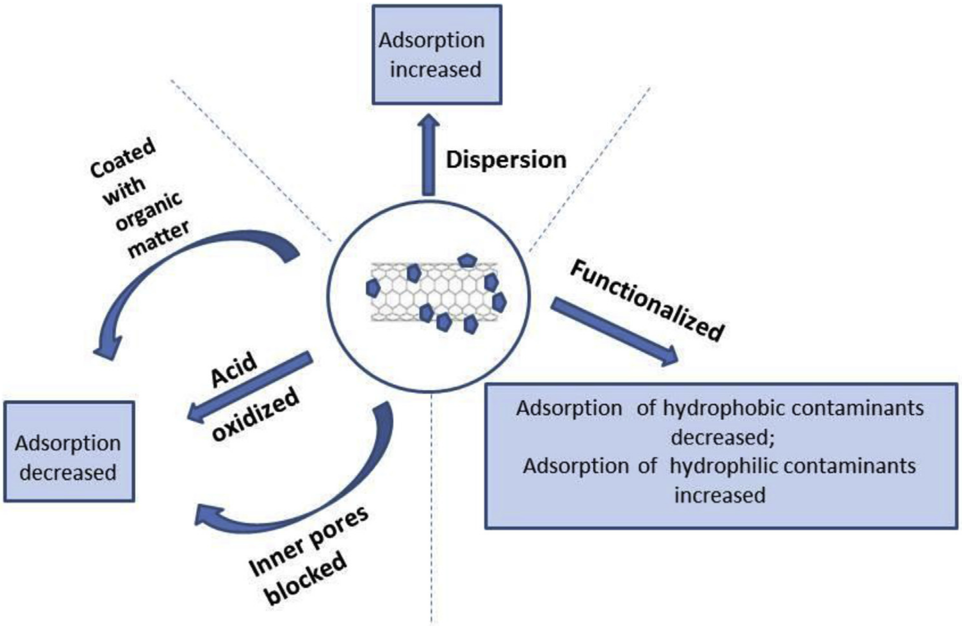

Fig. 5. Factors affecting the sorption of pollutants on CNTs.

can be desorbed or freely dissolved fraction. Sometimes, microorganisms can also utilize a part of adsorbed compounds by attachment or formation of biofilm on CNTs. This undoubtedly leads to the degradation possibility of adsorbed pollutants. In this case, the biodegradation of pollutants may not be significantly affected (Ren et al., 2018b; Xia et al., 2013).

The bioavailability of pollutants are related to their sorption-desorption behavior. Organic matter, properties of CNTs and properties of pollutants can affect the sorption-desorption behavior of pollutants. Some factors affecting the sorption on CNTs were showed in Fig. 5. These factors may affect the bioavailability of pollutants and result in effects on biodegradation (Kookana, 2010). In soil system, many organic components are correlated with the sorption-desorption behavior of pollutants, such as humic acid, soot and char (Li et al., 2013b). Natural organic matter (NOM) can change the suspension state of CNTs. 5 mg•L^{-1}NOM resulted in higher adsorption capacity of fluoranthene compared to addition of 10 mg L^{-1} NOM. At low concentration range, NOM can improve the dispersion of MWCNTs and increase the available sorption sites. Therefore, low concentration of NOM improved adsorption of fluoranthene by MWCNTs. However, NOM molecules and fluranthene may compete for sorption sites on MWCNTs. Thus, some sorption sites on MWCNTs were blocked by NOM and the sorption of fluoranthene was inhibited. NOM alleviated negative effects of CNTs on the bioavailability of pollutants. Furthermore, NOM can introduce some polar functional groups to the surface of SWCNTs, thereby reduced the sorption of phenanthrene on SWCNTs. Some researches showed that NOM may not only affect adsorption, but also have effects on desorption process. In the presence of NOM, PAHs were entrapped in nanopores or partition into NOM complexes. Adsorption of PAHs on silica particles was irreversible (Cui et al., 2011; Linard et al., 2015b).Carbonaceous materials have two possible types of sorption sites: external surface and pores inside. CNTs with larger specific surface area and higher porosity have higher adsorption strength to pollutants. Correspondingly, the bioavailability of pollutants decreases and their biodegradation is inhibited (Xia et al., 2010). Furthermore, different sorption site would lead to different desorption rate. When adsorbed on the surface and macropores, phenanthrene can be desorbed from MWCNTs. When adsorbed on the nanopores (mesopores and micropores),the desorption process was very slowly. And phenanthrene may be entrapped in micropores due to the interaction between phenanthrene and CNTs. As a result, increasing mesopore and micropore volume of CNTs resulted in less mineralzation of pollutans (Xia et al., 2010, 2013). However, most studies showed that CNT porosity could not be applied to explain adsorption completely (Pan and Xing, 2008). Adsorption can be affected by other CNT properties, such as surface function. It seems that the possible solute-sorbent interactions including: (a) hydrophobic interaction, (b) electrostatic attraction/repulsion, (c) hydrogen bond, and (d) π-π bonds (Pan and Xing, 2008; Suresh et al., 2012). Therefore, the addition of oxygen containing groups like –COOH to SWCNT makes it more hydrophilic, combined with the competitive effect of water molecules, resulting in less adsorption of biphenyl than pristine SWCNT (Qu et al., 2016). The reduction of adsorption capacity of resorcinol by acid-treated MWCNTs compared to untreated MWCNTs was due to the increase of electrostatic repulsion between solute and CNTs (Qiu et al., 2008). Since hydrophobic interactions are the main force, PAH with higher hydrophobicity (Kow) was more easily adsorbed on MWCNTs (Li et al., 2013b). Besides, reducing the bioavailability of organic pollutants by CNTs have two-sided effects. On the one hand, reducing the bioavailability of pollutants leads to fewer parts that can be obtained by organisms, thereby alleviating the environmental risk of toxicants. On the other hand, the reduction of available pollutants also reduced the microbial degradation. Reducing biodegradation may increase the persistence of pollutants in the environment and allowing pollutants to persist for longer time (Zhou et al., 2013; Zhu et al., 2016a). The worst case scenario is that CNTs may serve as the collector and facilitate the transport of organic contaminants (Pan and Xing, 2008; Riding et al., 2015).

3. Perspective and conclusion

Biodegradation is an important process of removal of pollutants in natural environment. It is closely related to the activity of microorganisms and enzymes. Except for some known environmental conditions, CNTs might also increase/decrease biodegradation. It depends on the concentration and properties of CNTs, physicochemical properties of microorganisms and pollutants, environmental condition. This made it more complicated to assess the effects of CNTs on biodegradation. The main mechanism by which CNTs affect biodegradation has not been identified. Some studies suggested that limited microbial activity leads to decreased biodegradation, while others suggested that reduced pollutants availability to microorganisms leads to decreased biodegradation. However, we can still draw some conclusions from current studies and propose some further research interests:

(1) CNTs inhibit microbial growth through a variety of toxic mechanisms. And microorganisms also have adaptive and protective mechanisms against such adverse effects. Various factors regulate the interaction between CNTs and microorganisms. However, many current studies were conducted in a model system with relatively high concentration of CNTs, which cannot fully reflect effects of CNTs in the actual environment. Except for effects on microbial activity, CNTs may affect the expression of microbial degradation genes. Whether CNTs have other mechanisms by which affect microbial degradation is not clear. Future studies need to be conducted in CNTs and pollutants co-exist sites and explore the detailed mechanisms by which CNTs affect biodegradation.

(2) There are some papers suggested that CNTs have an accelerating effect to the activity of redox reaction by enzyme due to following reasons: CNTs bind to the enzyme's activity center and participated in electron transfer process between substrate and enzyme. Thus, the activity of enzyme in oxidizing the reducing substrates are increased. However, some papers have completely different findings. It was suggested that CNTs inhibited the enzymatic oxidation of substrates by effects on the contact between enzyme and substrate.

(3) The effects of CNTs on biodegradation also related to the adsorption and desorption behavior of pollutants. By adsorption on CNTs, the availability of pollutants to functional microorganisms decreased. Accordingly, the biodegradation of pollutants decreased. Therefore, when CNTs are used as amendment in soil remediation, on the one hand, they can reduce the toxicity of pollutants. But on the other hand, CNTs may act as collectors and transporters of pollutants, leading to increased persistence of pollutants. So, more data need to reveal the effects of CNTs on biodegradation and persistence of pollutants, especially those with high sorption strength to CNTs. It is beneficial to assess ecological risks of CNTs entering the environment.

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