

REVIEW

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Biological Stability of Water-Based Cutting Fluids: Progress and Application

Lizhi Tang¹, Yanbin Zhang¹, Changhe Li^{1*}, Zongming Zhou², Xiaolin Nie³, Yun Chen⁴, Huajun Cao⁵, Bo Liu⁶, Naiqing Zhang⁷, Zafar Said⁸, Sujan Debnath⁹, Muhammad Jamil¹⁰, Hafiz Muhammad Ali¹¹ and Shubham Sharma¹²

Abstract

The application of cutting fluid in the field of engineering manufacturing has a history of hundreds of years, and it plays a vital role in the processing efficiency and surface quality of parts. Among them, water-based cutting fluid accounts for more than 90% of the consumption of cutting fluid. However, long-term recycling of water-based cutting fluid could easily cause deterioration, and the breeding of bacteria could cause the cutting fluid to fail, increase manufacturing costs, and even endanger the health of workers. Traditional bactericides could improve the biological stability of cutting fluids, but they are toxic to the environment and do not conform to the development trend of low-carbon manufacturing. Low-carbon manufacturing is inevitable and the direction of sustainable manufacturing. The use of nanomaterials, transition metal complexes, and physical sterilization methods on the bacterial cell membrane and genetic material could effectively solve this problem. In this article, the mechanism of action of additives and microbial metabolites was first analyzed. Then, the denaturation mechanism of traditional bactericides on the target protein and the effect of sterilization efficiency were summarized. Further, the mechanism of nanomaterials disrupting cell membrane potential was discussed. The effects of lipophilicity and the atomic number of transition metal complexes on cell membrane penetration were also summarized, and the effects of ultraviolet rays and ozone on the destruction of bacterial genetic material were reviewed. In other words, the bactericidal performance, hazard, degradability, and economics of various sterilization methods were comprehensively evaluated, and the potential development direction of improving the biological stability of cutting fluid was proposed.

Keywords: Cutting fluid, Microorganism, Bactericide, Sterilization

1 Introduction

Cutting fluids are widely used in machining processes, such as turning, milling, planing, grinding, and forming manufacturing processes, and they have functions, such as cooling, lubrication, rust prevention, and chip removal [1–3]. The use of cutting fluid is of great importance because it could reduce the cutting force and temperature during the cutting process and improve the surface quality of the workpiece and tool life [4, 5]. In accordance

with the composition of the cutting fluid, it could be divided into oil-based cutting fluid and water-based cutting fluid [6, 7]. Oil-based cutting fluid is prepared with oil as the base fluid. It has high biological stability but insufficient cooling performance [8, 9]. It is mostly used for slow processing or heavy-duty processing. For parts processing, the usage only accounts for a small part of the total usage of cutting fluid [10, 11]. The use ratio of water-based cutting fluid is as high as more than 90%, and water is used as the base fluid, which has good cooling performance [12, 13]. Meanwhile, to take into account the functions of lubrication, cleaning, and rust prevention, various additives are also added [14, 15]. However, the moisture in the water-based cutting fluid and the high

*Correspondence: sy_lichanghe@163.com

¹ School of Mechanical and Automotive Engineering, Qingdao University of Technology, Qingdao 266520, China

Full list of author information is available at the end of the article

trace elements in the additives could easily lead to the reproduction of microorganisms, hence the serious biological stability problems during usage [16, 17].

Water-based cutting fluid could breed many bacteria or fungi during use [18, 19]. The bacteria could decompose additives in the cutting fluid, destroy its stability, and reduce its performance. Fungi may also block the circulation system of the cutting fluid [20, 21]. The proliferation of bacteria could produce biofilms [22–24]. The existence of biofilms provides better conditions for bacteria to multiply, causing a vicious circle [25–27]. A more serious problem is that endotoxins, exotoxins, and bioaerosols produced by bacteria in water-based cutting fluids could cause respiratory diseases and affect the health of workers [28–30]. The harm of microorganisms to cutting fluids and human health has always been a problem in the field of mechanical processing [31–33]. Frequent replacement of cutting fluids due to microbial reproduction problems could inevitably cause a great waste of resources, contrary to the current green and sustainable development [34, 35]. Therefore, people have come up with various methods to inhibit the reproduction of microorganisms in the cutting fluid; the most commonly used is the use of biological bactericides. These bactericides could inactivate bacteria by destroying the cell membrane of microorganisms, destroying the structure of microbial proteins, and interfering with DNA synthesis [36, 37]. The types of bactericides commonly used in the industry include formaldehyde releasers, isothiazolinones, boric acids, and amines [38]. However, these kinds of bactericides are generally irritating and allergenic, and they could not avoid the harm to human health while killing bacteria [39, 40]. On the basis of the consideration of sterilization effect and human health, some scholars have explored new bactericides or sterilization methods used in cutting fluids. Different kinds of nanomaterials [41–43], transition metal complexes [44–46], and other new bactericides were studied, including physical sterilization methods, such as ultraviolet (UV) sterilization [47], ozone sterilization [48, 49], and fine-bubble [50] sterilization.

Low-carbon manufacturing is inevitable and the direction of sustainable development. Therefore, the use of environmental friendly methods to improve the biological stability of water-based cutting fluids is a current research hotspot. In this article, the mechanism of action of additives and microbial metabolites was introduced. Then, the denaturation effects of traditional bactericides on target proteins and their bactericidal efficiency were reviewed. The lipophilicity of nanomaterials and transition metal complexes and their influence on cell membrane penetration were discussed. The destructive effects of UV rays and ozone on bacterial genetic material and

their bactericidal effects were explored. Through the analysis, conclusions were drawn and prospects for the future development direction of the stability of water-based cutting fluids were elucidated. Figure 1 shows the structure of this article.

2 Cutting Fluid

Machining is widely used in automotive, aerospace, and other fields, and it is the basis of manufacturing industry. Cutting fluid is an indispensable element in the machining manufacturing industry [51–53]. The use of cutting fluid could reduce the cutting temperature, reduce the friction between the tool and the workpiece, extend the life of the tool, and improve the processing efficiency [54–56].

2.1 Function

Cutting fluid has the functions of cooling, lubrication, cleaning and rust prevention [57, 58]. Cooling effect: in the process of metal processing, the friction between the tool and the workpiece, the friction between the tool and the chip, the deformation of the metal, etc. could generate a huge amount of heat. Too much heat in the processing area could easily cause burns between the tool and workpiece, thus affecting the accuracy and smoothness of the workpiece surface [59–61]. In the metal processing process, the cutting fluid could realize the heat exchange effect in the metal cutting process through heat conduction and heat convection. Then, the heat in the cutting zone is taken away by continuous flow and vaporization to reduce the tool temperature [62–64], thereby improving the stability of the tool during the cutting process and the machining accuracy of the workpiece, reducing tool wear, and extending tool life [65–67].

Lubrication: during the machining process, the tool-workpiece and tool-chip interface could produce strong friction [68–70]. The cutting fluid penetrates into the

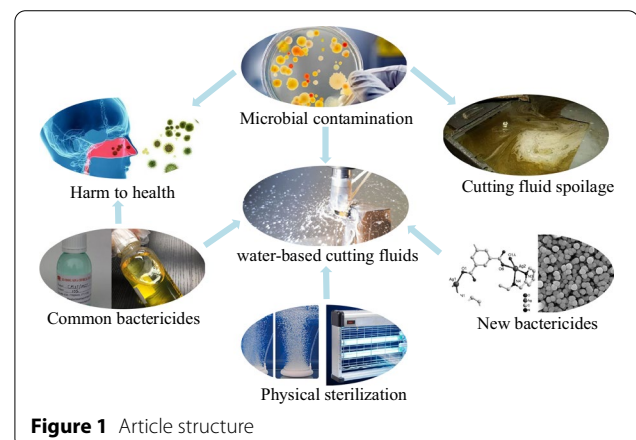


Figure 1 Article structure

cutting area to form a lubricating film (this kind of lubricating film could be divided into adsorption film and reaction film. The active material in the cutting fluid is adsorbed on the surface of the workpiece to form an adsorption film, and the additive in the cutting fluid chemically reacts with the workpiece to form a reactive film [71–73]), thereby reducing the friction between tool workpiece and tool chips, reducing energy consumption in the cutting process, reducing cutting force, and extending tool life [74–76].

Cleaning function: the chips produced in metal processing, dust, and oil in the air are adsorbed on the surface of tools and workpieces. This phenomenon has a certain effect on processing [77–79]. Cutting fluids could remove all kinds of dirt during the flow process to clean workpieces and tools [80, 81].

2.2 Classification

Cutting fluids could be divided into two groups in accordance with their composition: oil-based and water-based groups [82, 83], as shown in Figure 2.

The main components of oil-based cutting fluids include animal and vegetable oils and mineral oils. Oil-based cutting fluids were originally produced from animal and vegetable oils. However, because animal and vegetable oils are prone to corruption during use, they were gradually replaced by mineral oils [85, 86]. Oil-based cutting fluid has good lubricity. However, shortcomings exist, such as oil mist that is easy to produce and fire that is easy to catch during use [87]. Therefore, oil-based cutting fluids are mainly used for processing large or heavy parts. Meanwhile, because oil-based cutting fluid has good lubricating performance but poor cooling performance, it is generally used for low-speed cutting. Water-based cutting fluid is often used in high-speed cutting to ensure the machining accuracy.

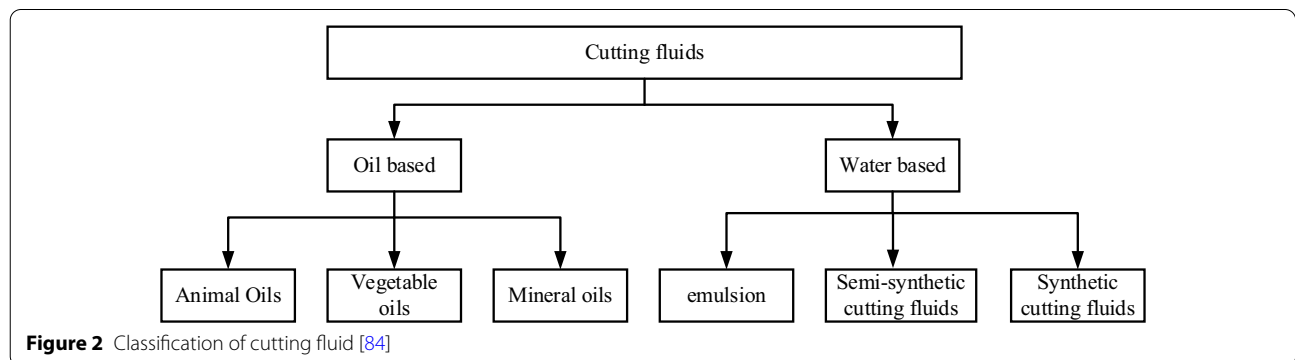
Water-based cutting fluids could also be divided into emulsions, semi-synthetic fluids [10, 11], and synthetic fluids. Emulsion is formed by mixing base oil and water

in a certain proportion. Its oil content is 60%–90%, the particle size is 1–10 μm, and its appearance is milky white [77, 88]. Emulsion has lubrication and cooling functions. However, its stability is poor, and it is easy to breed bacteria in the process of use [60]. Semi-synthetic fluid integrates the advantages of emulsion and synthetic fluid. Compared with emulsion, it adds more surfactants, which make the oil droplet size smaller, ranging from 0.05 μm to 0.1 μm. Therefore, it is more stable and less prone to deterioration. The appearance of semi-synthetic liquid is transparent or translucent. Therefore, observing the condition of the cutting area during machining is easy [85, 89]. The synthetic solution does not contain any oil. It uses other additives, such as water-soluble synthetic grease, to achieve its lubricating properties [65]. Its appearance is transparent, and it has excellent cooling performance. However, the machine tool is prone to rust after it is used [90], as shown in Table 1.

With the improvement of processing conditions; the call for energy saving and emission reduction; and the research on additives, such as lubricants, corrosion inhibitor, and bactericides, water-based cutting fluids have been developed rapidly due to their excellent cooling performance and low cost [91, 92]. In 2018, water-based cutting fluids have accounted for 90% of the total global demand for cutting fluids [12].

Table 1 The difference between different types of cutting fluids

Type	Oil content (%)	Particle size (μm)	Appearance
Oil-based	100	–	Transparent
Emulsion	60–90	>1	Milky
		0.1–1	Milky blue
Semi-synthetic	10–30	0.05–0.1	Translucent gray
		<0.05	Transparent
Synthetic	0	–	Transparent



2.3 Additives

Water-based cutting fluid is made by mixing mineral oil or synthetic oil with water in a certain proportion. It is a coolant and lubricant widely used in processing. Adding various additives to the cutting fluid is often necessary to enhance the performance of the cutting fluid and prolong its service life. Some examples, such as oily agents, extreme-pressure agents, emulsifiers, defoamers, corrosion inhibitors, and bactericides, are shown in Table 2.

The oily agent could form an adsorption film on the friction interface, thereby reducing the friction in the cutting zone. The commonly used oily agents include animal and vegetable oils, higher fatty acids, amines, and amide compounds. However, when the temperature of the friction interface increases, the activity of the molecules also increases. Therefore, the adsorption strength of the oil film decreases, resulting in the failure of the oil-based agent. Extreme-pressure additives contain organic compounds, such as phosphorus, sulfur, and chlorine. They react with metal surface and form chemical reaction film under high temperature and high pressure boundary lubrication. Therefore, they could induce a lubricating effect when the oily agent fails [14, 15].

After machining, a metal workpiece retains water on the surface, and it easily rusts after contacting with oxygen. Therefore, adding corrosion inhibitor to ensure that the workpiece does not rust in a period of time is necessary [94]. Corrosion inhibitors could be divided into anode corrosion inhibitors, cathodic corrosion inhibitors, and mixed corrosion inhibitors [95]. Anodic corrosion inhibitors could form oxide film on the surface of metal workpiece, thus delaying workpiece corrosion [96]. Cathodic corrosion inhibitors could be deposited on the cathode area to prevent electrons from flowing from the anode to the cathode [97, 98]. The mixed inhibitors could form a film on the surface of the workpiece to prevent corrosion. The mixed inhibitor is a polar material. Its head is adsorbed on the surface of the workpiece, and the nonpolar tail is closely arranged perpendicular to the workpiece, forming a tight protective film. In addition, the nonpolar tail could absorb hydrocarbons to increase

the thickness of the protective film, as shown in Figure 3 [94].

During the processing, due to the presence of surfactants in the cutting fluid, the cutting fluid tends to foam when it impacts the workpiece or the machine tool. The gas in the foam reduces the cooling performance of the cutting fluid. Thus, adding a defoaming agent is necessary. The defoaming agent plays an important role by inhibiting foam formation, thinning the foam film to the crack, and making the foam easier to fuse to accelerate bubble rupture.

Emulsifiers are mostly surfactants, one end of which is hydrophobic, and the other end is hydrophilic. It could form a molecular film at the interface of oil and water, reduce its surface tension, and make oil and water form a stable emulsion [99, 100], as shown in Figure 4.

Due to the emergence of various additives, the performance of water-based cutting fluids has been greatly improved. However, the cutting fluid is easily attacked by microorganisms. Every year, a large amount of cutting fluid is corrupted and deteriorated due to the proliferation of microorganisms, resulting in waste of energy and resources. Therefore, the microbial spoilage of cutting fluid needs to be solved urgently.

3 Biological Stability Issues in Water-Based Cutting Fluids

Water-based cutting fluids are extremely susceptible to microbial contamination. During the use of cutting fluid, the bacteria and microorganisms that exist in the water, on the workpiece, on the skin of the worker,

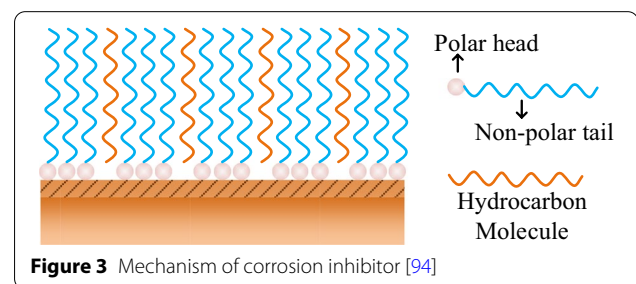
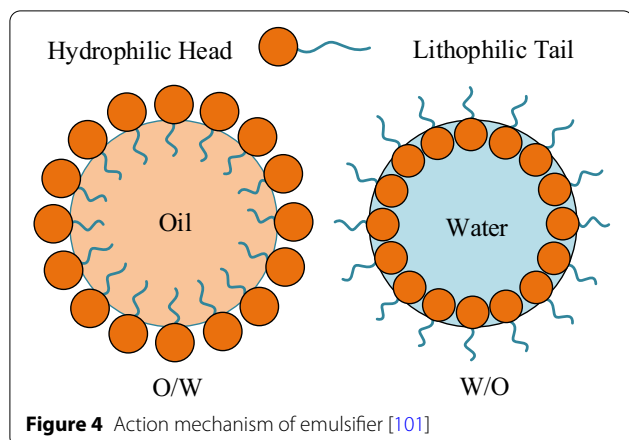


Figure 3 Mechanism of corrosion inhibitor [94]

Table 2 Additives [93]

Category	Additive	Effect
Oily agent, extreme pressure agent	Sulfur, phosphorus, chlorine and other organic compounds	Enhance the performance of the lubricating film
Corrosion inhibitor	Sodium nitrite, phenethanolamine	Prevent corrosion of the workpiece
Anti-foam	Dimethyl silicone oil, emulsified silicone oil	Reduce or eliminate foam
Emulsifier	Sodium Petroleum Sulfonate	Emulsion formation
Bactericide	Formaldehyde-releasers, isothiazolinone	Inhibit bacterial reproduction

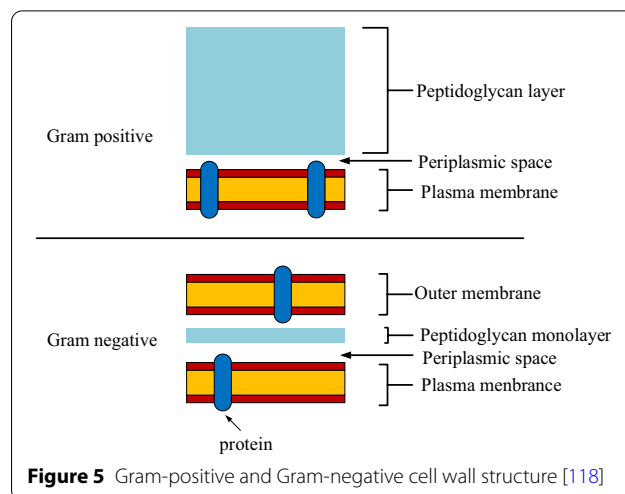


in the remaining liquid before the machine tool, and in the air are mixed into it [16]. The cutting fluid also contains organic matter needed for microbial reproduction; nitrogen, phosphorus, sulfur, and other trace elements in various additives; and water. The flow of cutting fluid makes it have more oxygen. All these phenomena provide favorable conditions for microbial reproduction and metabolism [102]. The metabolites of one microorganism in the cutting fluid may also become a food source for another organism to accelerate the propagation speed of microorganisms. In addition, the water-based cutting fluid in the machine tool is a complex system. The species and quantity of microorganisms change continuously during the use of cutting fluid [103].

3.1 Types of Microorganisms

The microorganisms in cutting fluid include bacteria and fungi. Bacteria could be divided into aerobic bacteria and anaerobic bacteria, such as *Escherichia coli*, *Staphylococcus aureus*, pneumococcus, *Salmonella typhi*, *Pseudomonas aeruginosa*, *Pseudomonas oleifera*, and sulfate reducing bacteria. Fungi are divided into yeast and mold, including *Penicillium*, cephalosporin, *Aspergillus*, and *Fusarium*. Facultative anaerobes are special and important biodegradants. When sufficient oxygen is present, facultative anaerobes behave like aerobic bacteria. When oxygen is not sufficient to support aerobic metabolism, they behave like anaerobic bacteria. Especially in biofilm community, facultative anaerobic bacteria consume oxygen, thus creating conditions suitable for anaerobic bacteria to survive [104].

In addition, because bacteria differ in accordance with the chemical composition, shape, and metabolic substances of their cell walls and respond differently to staining, they could also be divided into Gram-positive and Gram-negative bacteria [105]. Gram-positive bacteria have a thicker cell wall, and multiple peptidoglycan layers



are present within this cell wall. The cell wall of Gram-negative bacteria is thinner, with a characteristic outer membrane [50], as shown in Figure 5.

The number of microorganisms in cutting fluid is the key to affecting the cutting fluid performance and judge whether replacement of cutting fluid is necessary. Some scholars have found through research that the microbial concentration of contaminated cutting fluid ranges from 10^4 colony forming units (CFU)/mL to 10^{10} CFU/mL [106]. Shennan's study found that the bacteria in water-based cutting fluids were mainly Gram-negative bacteria with a microbial concentration of approximately 10^8 CFU/mL [103]. Some scholars further analyzed the 16S ribosomal DNA metagenome of microorganisms in used cutting fluid. They found that a large number of bacteria belonged to *Pseudomonas*, and the diversity of *Pseudomonas* bacteria was low [107, 108]. *Pseudomonas* is a kind of Gram-negative aerobic bacteria, which is the most common genus in cutting fluid, and it widely exists in soil and water environment [107].

In addition, the microbial species in the cutting fluid change with the degree of pollution. When the pollution is not serious, the spoilage bacteria are mainly *Pseudomonas* [103, 109]. When the microbial contamination reaches 10^8 CFU/mL, facultative anaerobes are the main bacteria. In the last stage of cutting fluid decay, the pH value of the cutting fluid decreases and the bacterial diversity increases. Various Gram-negative bacteria could be isolated from cutting fluid, including *Acinetobacter*, *Achromobacter*, and *Alcaligenes*. In addition, cutting fluid is contaminated by other common bacteria, such as Gram-positive bacteria (*Micrococcus*, *Staphylococcus*, *Streptococcus*, and *Bacillus*) and atypical mycobacteria [109–114]. Yeasts and filamentous fungi could also contaminate cutting fluid, but these are less abundant

(10^2 – 10^4 CFU/mL) [36, 115, 116]. Molds are mostly adhered to machine tool walls or pipes [117].

When the microorganisms in cutting fluid propagate to a certain extent, many microorganisms like to gather to form a multicellular community. This multicellular community is called biofilm [25–27], as shown in Figure 6. Biofilms appear as a slimy film or flocculus

in a liquid gathered on a moist wall surface, as shown in Figure 7. Biofilms also have complex structures, such as channels for fluid and nutrient transport, which could provide a sanctuary for microorganisms. Oxygen concentration gradient, organic matter concentration gradient, and pH value gradient could be formed at different positions of biofilm. Therefore, aerobic and anaerobic bacteria and acidophilic and acidophilic bacteria coexist. The interaction of microorganisms in the biofilm could also make the microbial resistance to bactericides 1000 times higher than before [119]. Some of them could go into dormancy until the external environment is suitable for their survival [120].

When the environment is suitable, the microbial species mentioned above could split once every 30 min or so. The number increases in geometric progression. When the machine is shut down, the cutting fluid is still. The growth of aerobic bacteria consumes the oxygen in the cutting fluid. When oxygen is not sufficient, anaerobic bacteria multiply. Anaerobic bacteria, such as sulfate-reducing bacteria and Citrobacter, could decompose sulfur groups in sulfate. Anaerobes generate hydrogen sulfide, which is dissolved in cutting fluid, by metabolism. When the machine tool is started again, hydrogen sulfide will be released, causing peculiar smell around the machine tool. As the reproduction speed of anaerobic bacteria is lower than that of aerobic bacteria, when the odor appears, it is a sign of severe spoilage of the cutting fluid, as shown in Figure 8.

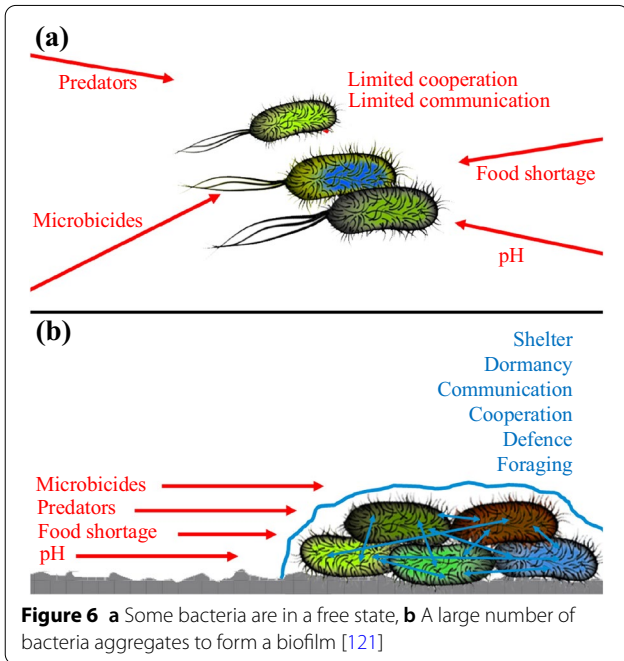


Figure 6 a Some bacteria are in a free state, b A large number of bacteria aggregates to form a biofilm [121]

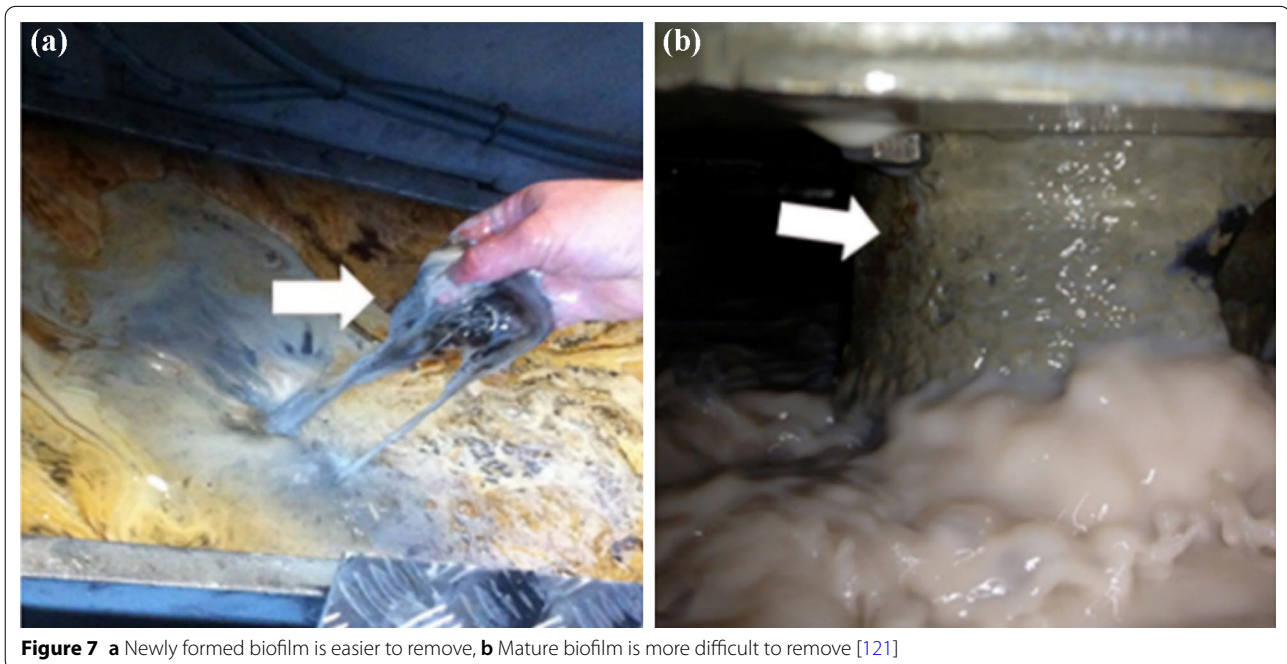
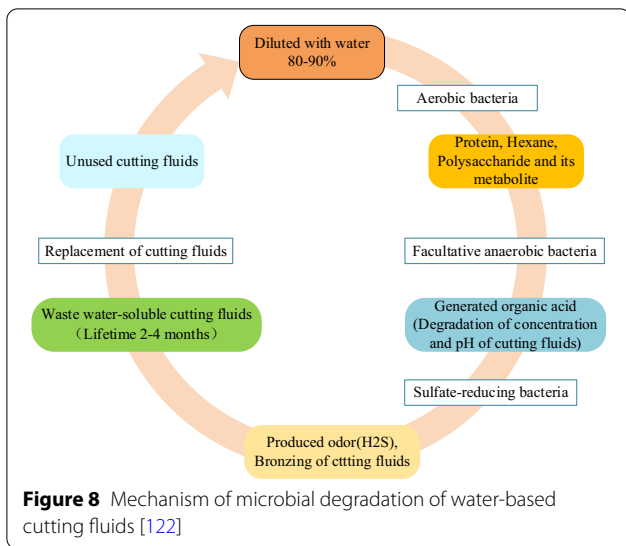


Figure 7 a Newly formed biofilm is easier to remove, b Mature biofilm is more difficult to remove [121]



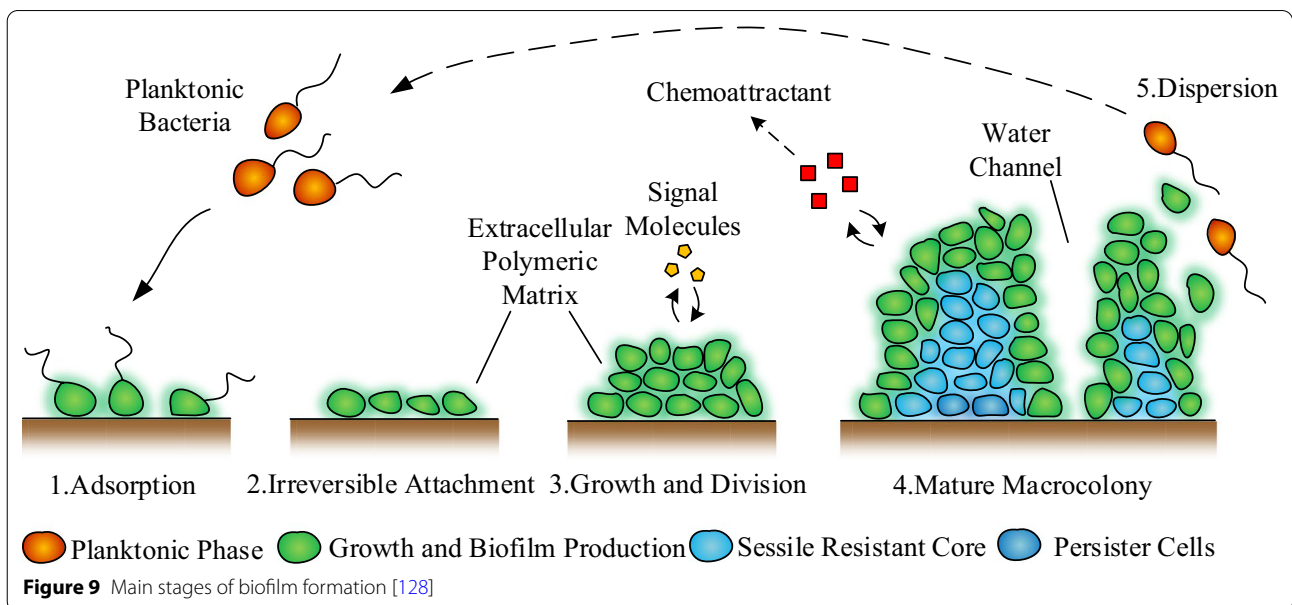
3.2 Microbial Influence

The microorganisms in cutting fluid could cause irreversible damage to the cutting fluid and machine tools. Bacteria decompose the emulsifier in the cutting fluid. When the emulsifier is consumed to a certain extent, the stability of the cutting fluid could be destroyed. Oil could precipitate out of this stable state, thereby affecting the lubricating performance of the cutting fluid. It could also reduce the PH value of the cutting fluid, thereby reducing its rust-proof performance [123]. It could make unsaturated bonds in the cutting fluid become saturated bonds, remove side chains from complex molecules, and shorten chain length [122], thus reducing the function of cutting

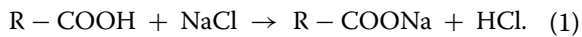
fluid. It could also cause malodor, reduce tool life (metal corrosion), increase friction heat, increase energy consumption, and reduce the surface finish of the workpiece [124].

Moulds and fungi could change the color of cutting fluid when they reproduce in large quantities. Lumps that block the circulation system of the cutting fluid, overload the circulation system, and have a certain effect on the filter and the liquid supply pipeline could also be present [124]. Meanwhile, molds and fungi undergo spore reproduction. Spore has very strong viability, high heat, and dry resistance. The mold must be removed with the spores to completely remove it. Thus, removing molds is more difficult than removing bacteria [125].

Microbes also aggregate to form biofilms, as shown in Figure 9. Biofilms are complex microbial communities growing in cutting fluids. They could be composed of various organisms, including Gram-positive and -negative bacteria and yeast. Biofilms could generate mucus, causing filter blockage, product contamination, and equipment damage [106]. Biomembranes could also create conditions that promote electrochemistry. Electrons could flow from the anode area covered by the biofilm to the cathode area on the metal surface, forming an electric current and corroding the metal. The common form of corrosion caused by microorganisms is pitting [126]. In addition, most of the microorganisms produce acidic metabolites (mainly C1–C6 carboxylic acids) [127]. These organic acids are not very corrosive. However, they could react with inorganic chlorides to form weak organic bases and strong



inorganic acids. They cause metals to be further corroded, especially hydrochloric acid (Eq. (1)) [127]:



In addition, the microorganisms in cutting fluid could have some effects on human physical health. The damage to workers' health is mainly allergic diseases. The Mycobacterium cells and their metabolites in cutting fluid may cause a series of inflammations ranging from mild rhinitis to fatal allergic pneumonia [129]. Hydrogen sulfide, the metabolite of anaerobic bacteria, is an odorous and highly toxic gas. It could cause toxicity to human lung, heart, and other organs. Various pathogens may also cause infection in workers' wounds [129].

Cutting fluid produces bio-aerosol during use. Bio-aerosols are air-suspended particles containing organisms or their metabolites. These particles are usually toxic or sensitive [130]. Toxic aerosols are further divided into exotoxins and endotoxins. Exotoxins are secreted by organisms, mainly diffusion proteins secreted by Gram-positive bacteria into the surrounding medium. Endotoxin is a structural component of organisms and an inducer of inflammatory cytokines [131], as shown in Figure 10. The most common endotoxin that workers are exposed to is a lipopolysaccharide. It is found in the outer membrane of the cell wall of Gram-negative bacteria. Exposure of endotoxin produced by cell wall rupture to the air may cause respiratory disorders and narrow the human bronchial tubes. It could increase the release of pro-inflammatory cytokines, causing workers to produce fever and respiratory symptoms [132]. It could also cause acute or chronic lung inflammation, including chronic sputum expectoration, lung function decline, fatigue, atherosclerosis and even toxic shock [28, 29].

The hazards caused by microorganisms are not estimable, and measures must be taken to control the propagation of microorganisms in cutting fluid. Among them, the main factors affecting microorganism multiplication are pH value, temperature, oil content, and water quality of water-based cutting fluids. Therefore,

to prevent the harm caused by microorganisms, the following points must be started. (1) Dilute the cutting fluid by using tap or demineralized water, with minimal use of water with high hardness. (2) Try to avoid the machine tool shutdown for a long time to keep the cutting fluid under flow and avoid heavy multiplication of anaerobes. (3) Clean the machine tools and their surroundings before cutting fluid injection to avoid carrying bacteria at the beginning. (4) Add a fungicidal mold inhibitor to the cutting fluid and replenish it in a timely manner. Among them, the most common and effective method to control the growth of microorganisms in cutting fluids is to use bactericides. It could control microorganisms within a certain number range, thus extending the useful life of cutting fluid.

4 Bactericides in Cutting Fluid

4.1 Commonly Used Bactericides

The effect of Bactericides on microorganisms is generally divided into three stages: physicochemical absorption of the bactericides on the microbial surface, penetration of the bactericides into the cells, and the effect of the bactericides on the target site. However, not all bactericides need to penetrate inside the cell to function. Part of the bactericides could act on one or more target sites, such as cell membranes, intracellular proteins, and nucleic acids (NAs). In addition, due to the diversity of microorganisms, each bactericide has its own sterilization mechanism, such as obstructing bacterial respiration, affecting bacterial metabolic processes, inhibiting protein synthesis, damaging the cell wall, and impeding NA formation (Table 3).

The bactericides used in cutting fluid should meet the criteria of having broad spectrum, low concentration availability, stability, noncorrosive to metals, noncontaminating environment, cheap, not causing intensive hazards to organisms outside the target, and not making the target organisms drug resistant [36].

The two main bactericides commonly used in industry are formaldehyde releasers and isothiazolinone. Formaldehyde releasers could release highly volatile formaldehyde. In addition, formaldehyde changes the structure of proteins through denaturation and interacts with

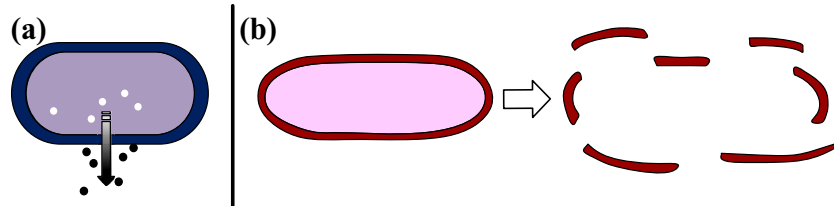


Figure 10 a Exotoxin, b Endotoxin [121]

Table 3 Mechanism of different kinds of organic molecules to kill microorganisms [36]

Types of bactericides	Mechanism
Acid	Interaction with cell membrane
Alcohol	Denature protein and dissolve cell membrane
Formaldehyde and formaldehyde-releasers	Combine with NH ₂ group and affect protein and nucleic acid
Biguanides	Interact with cell membrane and affect protein and nucleic acid
Isothiazolinone	Inhibit enzyme
Phenolic compounds	Denature protein and modify cell membrane

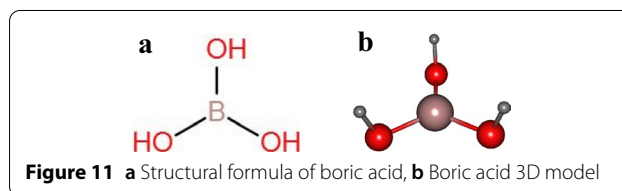
bacterial NAs through alkylation reactions to inhibit the excessive reproduction of bacterial and fungal populations [133], including *Pseudomonas* species, sulphate reducing bacteria, *Fusarium* species, cepacia species, and *Candida* species [124]. Isothiazolinone-based biological bactericides have the advantage of not relying on the mechanism of action of formaldehyde. It mainly acts on bacterial membranes and proteins [134]. It has a strong sterilization effect on sulfate-reducing bacteria and a poor inactivation effect on *Pseudomonas* and mycobacteria [36].

Formaldehyde releasers have a fast sterilization speed, but poor stability and strong irritation to the skin. Isothiazolinone has strong stability in cutting fluids, and it could quickly kill microorganisms. However, isothiazolinones are skin sensitizers that could cause contact dermatitis [39], and their use has been reduced [36]. Other chemical categories include phenols, pyridinone [121], iodine with propynyl carbamate, and sodium pyrithione [135].

Phenolic substances are antibacterial agents that act on cell membranes. They inactivate bacteria by interacting with the cell membrane surface to disintegrate the cell and release the substance inside the cell. Phenolics could also coagulate cell fluid, cause cell death, or inhibit cell growth [136, 137]. In addition, phenolic bactericides could inactivate acid-resistant bacteria more effectively than other bactericides. However, the chlorine contained in its component produces a special odor, and it is difficult to remove in the waste liquid [138]. Therefore, although phenolic resins have been registered for cutting fluids, they are still restricted by wastewater discharge regulations. Iodopropynylcarbamate is a broad-spectrum mold control agent with rapid bactericidal effect. However, its water solubility is poor, and its thermal stability is general. The sodium pyrithione antifungal agent has good water solubility and stability in cutting fluid, but its sterilization speed is slow [139].

4.2 Boric Acid and Formaldehyde-Releasers

Boric acid and formaldehyde releasers are commonly used bactericides in cutting fluids in industry. Boronic



acid has a molecular formula of H₃BO₃, and it is an inorganic acid. Its structural unit is a planar triangle [140], as shown in Figure 11. The atomic number of boron in the periodic table is 5, and the valence electron structure is 2S²2P¹. Its number of valence electrons is less than the number of valence orbitals, and it has electron loss [141]. Therefore, it could easily react with the hydroxyl in organic compounds (form borate after dehydration) and form boric acid monoester, diester, triester, and tetra-substituted spiro ring structure [140].

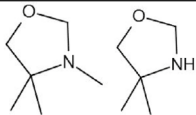
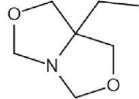
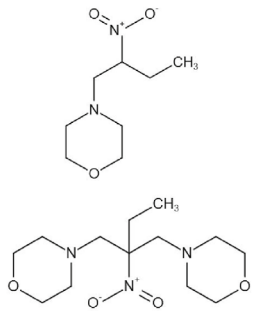

Formaldehyde is a colorless gas with a pungent odor. Formalin is a 37%–40% aqueous formaldehyde solution. Formaldehyde releasers exhibit a wide range of antibacterial activities, and they are by far the most popular and effective bactericides applied in cutting fluids. Anton C. de Groot et al. listed the CAS numbers, chemical structures, and molecular formulas of several commonly used formaldehyde releasers in water-based cutting fluids (Table 4) [142].

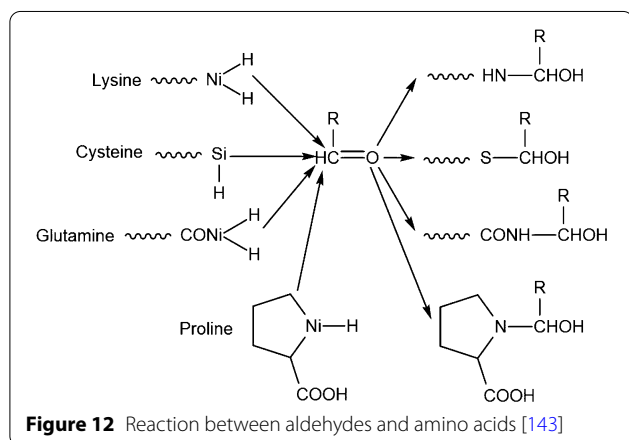
4.2.1 Sterilizing Mechanisms

Boric acid is an enzyme inhibitor that could block enzymes in phospholipid metabolism. The boron in borate is an electron-deficient element that could combine with external electrons. It could change the permeability of the cell membrane or cell wall by binding to the negatively charged cell surface, causing the cell to rupture and die.

Formaldehyde releasers control microbial reproduction by releasing formaldehyde. Their target is the amino acid or protein of bacteria. These are usually enzymes or other proteins or important components that undertake the main functions of the cell. Its release rate of formaldehyde

Table 4 Formaldehyde-releasers [142]

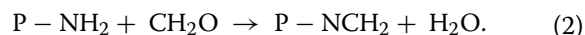
Name	CAS	Molecular formula	Chemical structure
Bioban®CS-1135	51200-87-4; 75673-43-7	C ₆ H ₁₃ NO; C ₅ H ₁₁ NO	
Bioban®CS-1246	7747-35-5	C ₇ H ₁₃ NO ₂	
Bioban®P-1487	37304-88-4	C ₁₃ H ₂₅ N ₃ O ₄ ; C ₈ H ₁₆ N ₂ O ₃	
1,6-Dihydroxy-2,5-dioxane	3586-55-8	C ₄ H ₁₀ O ₄	



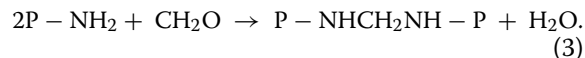
has a relationship with the properties of the bactericides, its concentration, the pH value of cutting fluid, temperature, and the degree of microbial contamination [132]. Aldehydes belong to the group of electrophilic addition active species. Given the lack of electrons at its carbonyl carbon atom, it could react with cell nucleophiles to exert antibacterial activity. The nucleophilic reaction with aldehydes in cells are amino and thiol groups, amino acid, or protein amide groups. These are the components of enzymes, as shown in Figure 12.

The reaction process of formaldehyde with amino group on protein is as follows [144].

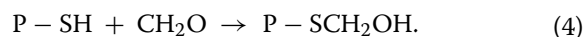
In acid or neutral solutions:



In alkaline solution:



The reaction of sulfhydryl group on protein molecule with formaldehyde is as follows:



4.2.2 Bactericidal Effect

Li et al. studied the germicidal efficacy of boric acid bactericides (ammonium borate) and formaldehyde releasers (triazine) with different concentrations. Before the experiment, the total number of bacterial colonies was more than 10^7 CFU/mL, and the total number of fungal colonies was more than 10^3 CFU/mL. The test results are shown in Figure 13.

The experiments showed that the antibacterial ability of ammonium borate and triazine bactericides was positively correlated with the concentration. The inactivation effect on bacteria was stronger than on fungi. The ammonium borate concentration of 5% showed enhanced sterilization performance. Triazines have a fast sterilization speed, but the inhibition time of bacteria and fungi after

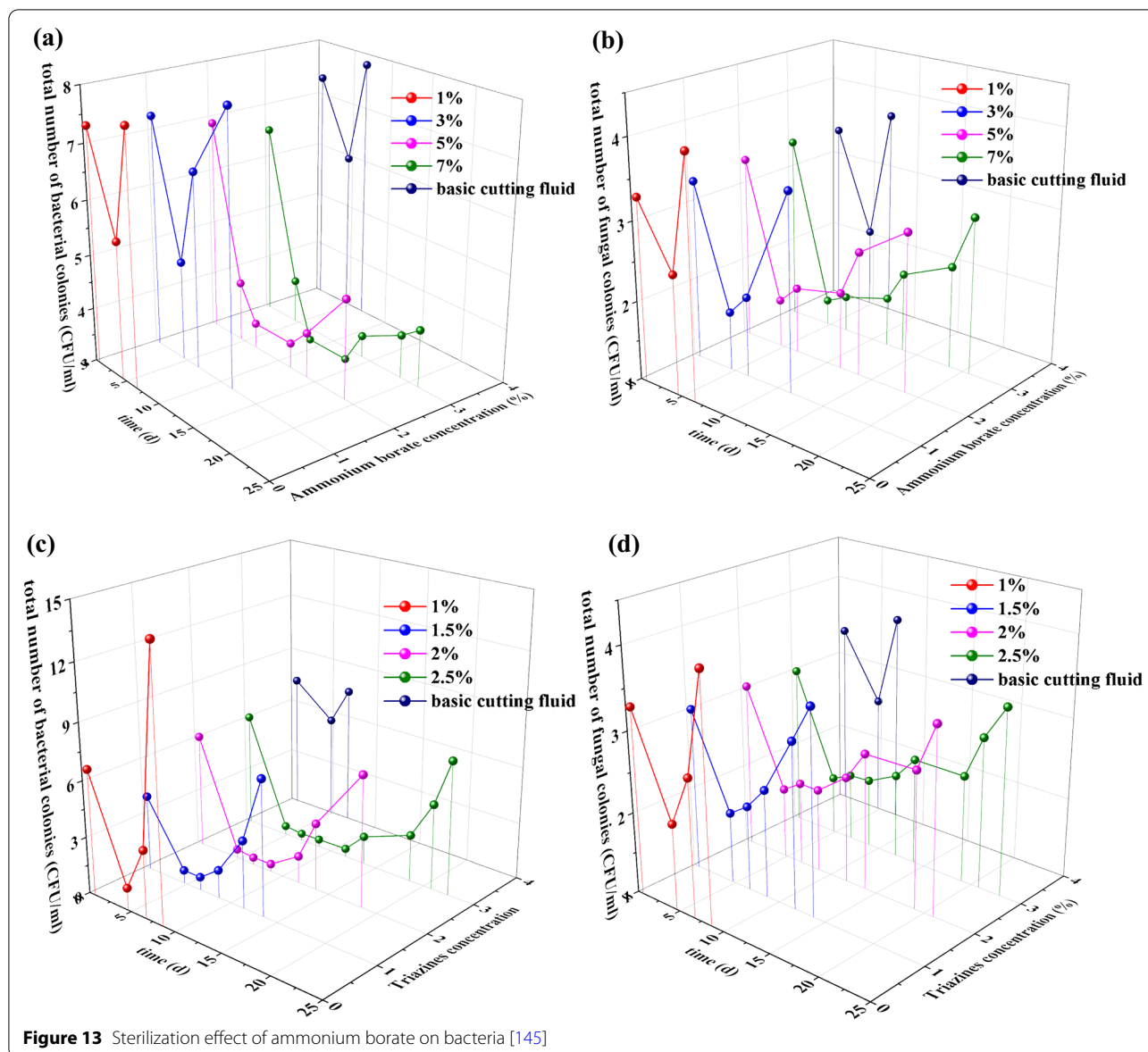


Figure 13 Sterilization effect of ammonium borate on bacteria [145]

sterilization is not long enough. The number of fungal colonies quickly recovers to the initial value.

4.2.3 Harm to the Environment and Workers

Boron is a common element in rock, soil, and water. Inhalation of boric acid or borate could cause respiratory irritation. Researchers found that when the average intake of boric acid was 4.1 mg/L, the eyes were stimulated; the mouth, nose, or throat dried; and the throat suffered from pain and coughing. [146]. In addition, boron is a dynamic trace element. It affects the metabolism or utilization of many substances involved in life, including calcium, copper, magnesium, nitrogen, glucose, triglycerides, reactive oxygen species, and estrogen.

Through these effects, boron could affect the function or composition of multiple human systems including, the immune system, blood, brain, and bones. EU regulators consider boric acid to be Class 1B reproductive toxic. The World Health Organization stipulates that the maximum concentration limits of boron in industrial drainage and drinking water are 10 and 1 mg/L, respectively [147].

Due to the presence of formaldehyde releasers in cutting fluid, workers who frequently touch with cutting fluid are prone to occupation dermatitis. The incidence rate of hand eczema was reported to be 20%–25% in 3 years. Formaldehyde is also a strong sensitizer, and it is a common cause of allergic contact dermatitis. In the United States, the sensitization frequency of this

allergen is approximately 8%–9%. The European plaque test results reported that the sensitization frequency is between 2% and 3%, and the Spanish sensitization frequency is 1.61% [148]. Irritative contact dermatitis is more common than allergic contact dermatitis. Anton de Groot counted the sensitization rates of different kinds of formaldehyde releasers [124, 149].

5 Exploration of New Bactericides

In addition to the existing bactericides used in cutting fluids, the bactericides used in other fields were discussed to explore more possibilities for various bactericidal materials to be applied in cutting fluids, including nanomaterials and transition metal complex used in medicine, animal and plant science, and other fields.

5.1 Nanomaterials

Bacteria could develop resistance to bactericides by secreting enzymes that degrade the bactericides, thus altering the permeability of the cell membrane and the target proteins of the bactericides [42, 150]. Therefore, the sterilization performance of the bactericides is greatly reduced after a period of application. Other alternatives must be considered. Nanoparticles are small in size, and they could easily pass through cell membranes. Nanoparticles enter the cell faster than the cell removes the nanoparticles. Therefore, nanoparticles could accumulate in the cell, thereby hindering the physiological process of the cell and destroying the cell structure and function [151]. The use of nanomaterials could thus be considered as an alternative to bactericides. Some scholars have found that the antibacterial activity of nanomaterials is related to shape, size, electronic structure, and surface properties [42]. Bacteria could be inactivated through various mechanisms, including cell membrane rupture, inhibition of nutrients from entering the cell, and blocking of cells from attaching to solid surfaces [41, 42]. Various nanomaterials are known to produce bactericidal effects against Gram-negative and -positive bacteria, such as Cu [152], CuO [153, 154], Ag [152, 155], silver phosphate [156], graphene-derived materials, and carbon nanotubes [157]. The effect of nanoparticles on Gram-negative bacteria is considerably more significant than that on Gram-positive bacteria [158].

Since the ancient times, people have known that silver and its compounds have strong antibacterial and bactericidal effects. They have broad-spectrum antibacterial activity against bacteria and fungi [159–161]. Compared with other metals, silver is more toxic to microorganisms than to mammalian cells [162, 163]. Humberto H. Lara found that silver nanoparticles could inhibit the formation of biofilms by destroying the cell wall of *Candida albicans*. They could also disrupt the membrane potential

to create small pores in the cell membrane, thereby triggering the leakage of ions and other substances in the cell to kill the bacteria. He proved their sterilization activity against *Candida albicans* through experiments [164]. Anna Ogar studied the inhibitory effect of silver nanoparticles on fungi. Experimental results showed that their inactivation effect on fungi depends on the concentration and release rate of Ag ions. The author also found that silver nanoparticles with a concentration of 30–200 mg/L could significantly inhibit the growth of fungi [165]. Melisa Moneris explored the sterilization ability of silver ion nanocomposites against *P. aeruginosa* [166]. Nasrollahi studied the inhibitory effects of silver nanoparticles on *Candida albicans* and *Saccharomyces cerevisiae* and found through experiments that they have a strong inactivation effect. The 50% minimum inhibitory concentration values for *Candida albicans* and *Saccharomyces cerevisiae* were 0.5 and 4 mg/mL, while the 90% minimum inhibitory concentration values were 2 and 32 mg/mL, respectively. The reason may be that nanosilver particles could inactivate bacteria by destroying the integrity of the membrane, affecting the permeability of the membrane, and reducing the activity of enzymes [163]. In the antibacterial activity test, a certain amount of nanoparticles was added to the cutting fluid. The smaller the particle size of the nanoparticles is, the more contact area with the cutting fluid, hence the better the antibacterial performance. Vijay C Verma studied the synthesis of nanosilver and its antibacterial activity against *C. albicans*, *Pseudomonas fluorescens* and *E. coli*. Its average minimum inhibitory concentration (MIC) for *C. albicans* was 5.83 µg/mL, and the minimum bactericidal concentration (MBC) was 9.7 µg/mL [167]. Yen San Chan studied the antibacterial properties of synthetic silver nanoparticles (AgNPs) against *S. aureus*, *E. coli*, *A. niger*, and *C. albicans*. The results showed that AgNPs have strong antibacterial and antifungal activities [168].

Suresh studied nickel oxide (n-NiO) and nickel oxide (f-NiO) nanoparticles functionalized with the surface of 5 amino-2-mercaptobenzimidazole (AMB) and the antibacterial activity of Ag₃O₄ nanoparticles and AMB surface functionalized Ag₃O₄ nanoparticles against *P. aeruginosa*, *S. aureus*, and *A. niger*. The experimental results showed that the antibacterial and antifungal activities of the functionalized nickel oxide nanoparticles were greater than those of the unmodified non-functionalized nickel oxide nanoparticles. The MIC of f-NiO was 20 mg/mL, and the MIC of n-NiO was 80 mg/mL. The antibacterial and antifungal activities of non-functionalized Ag₃O₄ nanoparticles were larger than those of functionalized Ag₃O₄ nanoparticles. The stronger antibacterial effect of the functionalized nickel oxide nanoparticles may be due to the enhanced

dispersion of the nanoparticles. The functionalized Ag_3O_4 may be due to the increase in particle size that reduces the antibacterial effect [158, 169].

Pooja Devi studied the synthesis of silica/silver core-shell nanoparticles and bactericidal activity against *Bacillus subtilis* (Gram-positive) and *E. coli* (Gram-negative) and found that the synthesized nanoparticles have inhibitory effects on both bacteria. The antibacterial ability of the experimental materials is related to the proportion of silver on the surface of the silicon core. When the mass fraction of silver was 0.5%, the MIC was 250 $\mu\text{g}/\text{mL}$, and when the mass fraction of silver was 15%, the MIC was 7.8 $\mu\text{g}/\text{mL}$ [170].

Graphene oxide (GO) could destroy cell membranes to kill bacteria through chemical reactions. Reduced GO (RGO) destroys cell membranes through mechanical stress to kill bacteria. Iman Sengupta investigated experimentally the effect of GO and reduced RGO on *S. aureus* and *P. aeruginosa*. The experimental results found that the inhibition rates of GO against *S. aureus* and *P. aeruginosa* were 93.7% and 48.6%, respectively, while the inhibition rates of RGO were 67.7% and 93.3%, respectively [42].

Muhammad Arshad studied the synthesis of zinc-doped silica nanoparticles synthesized in three different solvents (acetonitrile, n-hexane, and isoamyl alcohol), along with their antibacterial and antifungal properties. He mainly studied the biological activity against *B. subtilis* and *E. coli* and the bacteriostatic activity against *Candida* and *A. niger* [171].

Copper ions could damage cell membranes by being adsorbed to the bacterial cell surface, thus curing protein structure or altering enzyme function [172–174]. Its antibacterial mechanism is mainly attributed to the strong adsorption of copper ions by bacterial cells. This adsorption effect has a great relationship with copper ion concentration [175]. Ramesh synthesized a simple, low-cost, and environmental friendly Cu_2O nanoparticle. He used *E. coli* as a model to study the antibacterial properties of nano Cu_2O nanoparticles against Gram-negative bacteria. An antibacterial test was performed on *E. coli* on agar plates containing different concentrations of nanoparticles. The initial number of bacterial colonies on threagar plates was approximately 10^6 CFU/mL. Figure 14 shows the variation in the number of bacterial colonies as a function of nano- Cu_2O concentration. When the concentration of these particles was 10 $\mu\text{g}/\text{mL}$, the growth of bacteria was inhibited by 65%. The number of bacterial colonies grown on plates with nanoparticles exceeding 30 $\mu\text{g}/\text{mL}$ decreased significantly, and the nanoparticle concentration of 50–60 $\mu\text{g}/\text{mL}$ could inhibit the growth of bacteria by 100% [176].

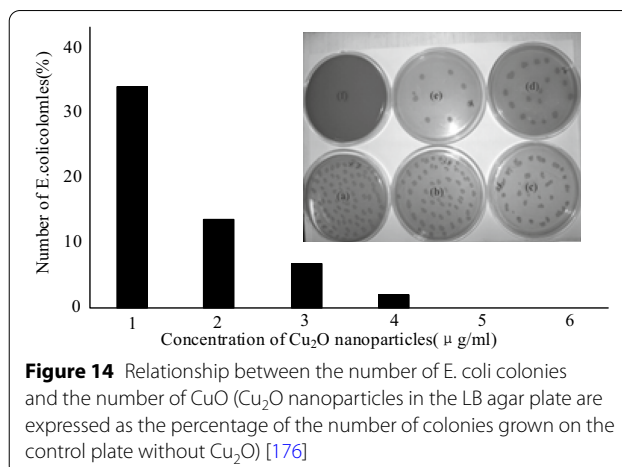


Figure 14 Relationship between the number of *E. coli* colonies and the number of CuO (Cu_2O nanoparticles in the LB agar plate are expressed as the percentage of the number of colonies grown on the control plate without Cu_2O) [176]

Table 5 summarizes the influence of different nanomaterials and their particle size on the sterilization performance.

As shown by the above studies, nanomaterials mostly achieve the inactivation of microorganisms by disturbing the potential of the cell membrane and disrupting the cell membrane. As Gram-positive bacteria are structurally different from Gram-negative bacteria, their multiple peptidoglycan layers could reinforce the stability of the cell membrane. Thus, the effect of nanomaterials on the action of Gram-negative bacteria should be higher than that on Gram-positive bacteria. In addition, the smaller the particle size of nanoparticles is, the more favorable it is to pass through the cell membrane, combining with other substances inside the cell. Therefore, a stronger bactericidal capacity could also be expected.

5.2 Transition Metal Complex

Metals are good conductors of electricity and heat, and they could form ionic and ionic bonds with nonmetals. Atoms in metals could easily lose electrons to form cations surrounded by free electrons. Thus producing conductive and antibacterial effects [177]. Heavy metals could be toxic to bacteria. This toxicity may be due to their chemical affinity with macromolecular thiol groups [44, 45]. Several modes of action of heavy metals are shown in Figure 15 [178].

The complexation of bactericides with transition metals could improve the biological activity of the original bactericides. Jie Li synthesized two Cu (II) complexes $[\text{CuL}_1^2(\text{OAc})_2] \cdot \text{MeOH}(1)$ and $[\text{CuL}_2^2(\text{OAc})_2]$ by using commercial bactericides paclobutrazol (L^1) and diclozole (L^2) as ligands (2). Ligand L^2 has C=C bond and 2,4-dichlorophenyl group, and it has a higher level of synergy. Therefore, complex 2 has stronger antifungal activity. Experimental studies on the synergy

Table 5 Nano material sterilization performance

Material	Size (nm)	MIC (mg/mL)	Zone of inhibition (mm)	Percentage inhibition	Ref. No.
AgNPS	50–80	0.3×10^{-4} –0.047	8.1–36.4		[166]
			<i>S. aureus</i> : 1.4–2.0; <i>E. coli</i> : 0.8–1.8 9–16		[168]
		<i>C. albicans</i> : MIC50=0.5, MIC90=2; <i>S. cerevisiae</i> : MIC50=4, MIC90=32			[163]
	10–25	5.8×10^{-3}			[167]
n-Ag ₃ O ₄	18		<i>S. aureus</i> : 13–16; <i>P. Aeruginosa</i> : 13–16		[169]
f-Ag ₃ O ₄	30		<i>S. aureus</i> : 7–8; <i>P. Aeruginosa</i> : 7–11		
n-NiO	16		<i>S. aureus</i> : 5–6; <i>P. Aeruginosa</i> : 6–7		[158]
f-NiO	20		<i>S. aureus</i> : 7–15; <i>P. Aeruginosa</i> : 12–17		
Cu ₂ O		MIC50=0.01 MIC90=0.055			[176]
SiO ₂	50–100	<i>B. subtilis</i> : 6%–2%; <i>E. coli</i> : 4.5%–1%			[171]
SiO ₂ +Ag	16–35	<i>B. subtilis</i> : 0.016–0.500; <i>E. coli</i> : 0.008–0.25			[170]
GO				<i>S. aureus</i> : 97.3% <i>P. Aeruginosa</i> : 48.6%	[42]
rGO				<i>S. aureus</i> : 67.7% <i>P. Aeruginosa</i> : 93.3%	

Note: *Staphylococcus aureus*: *S. aureus*; *Pseudomonas aeruginosa*: *P. Aeruginosa*; *Escherichia coli*: *E. coli*; *Bacillus subtilis*: *B. subtilis*; *Candida albicans*: *C. albicans*; *Saccharomyces cerevisiae*: *S. cerevisiae*; non-functionalized silver oxide nanoparticles referred as n-Ag3O4, functionalized nanoparticles as f-Ag3O4; non-functionalized nickel oxide nano-particles are referred to as n-NiO, functionalized nickel oxide nanoparticles as f-NiO; graphene oxide: GO; reduced GO: rGO

between Cu²⁺ and ligands and theoretical studies on the electronic structure of the complexes showed that the increase in active sites for copper ion, the synergy between copper ion and ligands, and the enhanced permeability through microbial cell membranes all contribute to the enhanced bactericidal performance [179].

VM Farzaliyev studied Schiff bases and their complexes with transition metals (Cu²⁺, Ni²⁺, and Co²⁺) against lactic acid bacteria, *P. aeruginosa*, *A. niger*, *Cladosporium resinosum*, *Penicillium*, *S. globosa*, and *Trichoderma viride*. The antibacterial performance and synthesis scheme is shown in Figure 16. The experimental results showed that the antibacterial properties of Schiff bases and their metal complexes reached the level of the selected standard bactericides, and in some cases, even exceeded the standard bactericides. In addition, due to the presence of additional dimethylamine fragments in the molecule, 4-dimethylamino-1 benzy-laniline and its complexes with Cu²⁺, Ni²⁺, and Co²⁺ demonstrated low concentrations (0.25%–0.5%), sterilization, and bactericidal properties [180].

Fatullayeva synthesized bis-(3,5-di-tert-butyl-salicylic acid) hydrazone and its analogues of dihydrazine succinate. He obtained the complexes of Mn (II) and Fe (II) with these ligands and found through tests that the obtained compounds have high bactericidal and bactericidal activities [181]. Rahimova synthesized the complexes of Cu (II) and Ni (II) with N,N-bis (p-dimethylaminobenzyl) diaminopropane, analyzed their antibacterial properties, and found that the synthesized compounds had strong bactericidal and bactericidal activities [182].

Under the chelation of transition metal and ligand, the polarity of the metal ion is greatly reduced due to the overlap of the ligand orbital and the partial participation of the positive charge of the metal ion and the donor base [183]. In addition, the compounding process could increase the lipophilicity of the central metal atom, beneficial for the complex to penetrate the lipid layer of the microbial cell membrane [184]. Table 6 summarizes the bactericidal properties of some transition metal complexes in the existing literature. A rule could be drawn

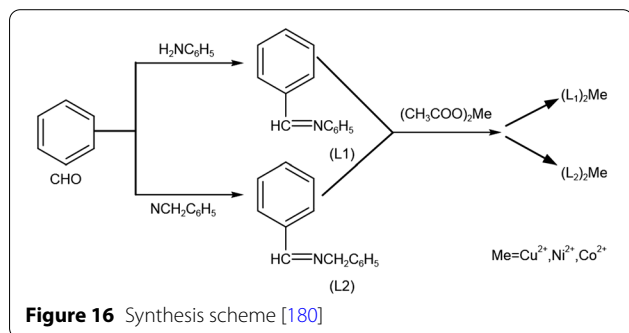
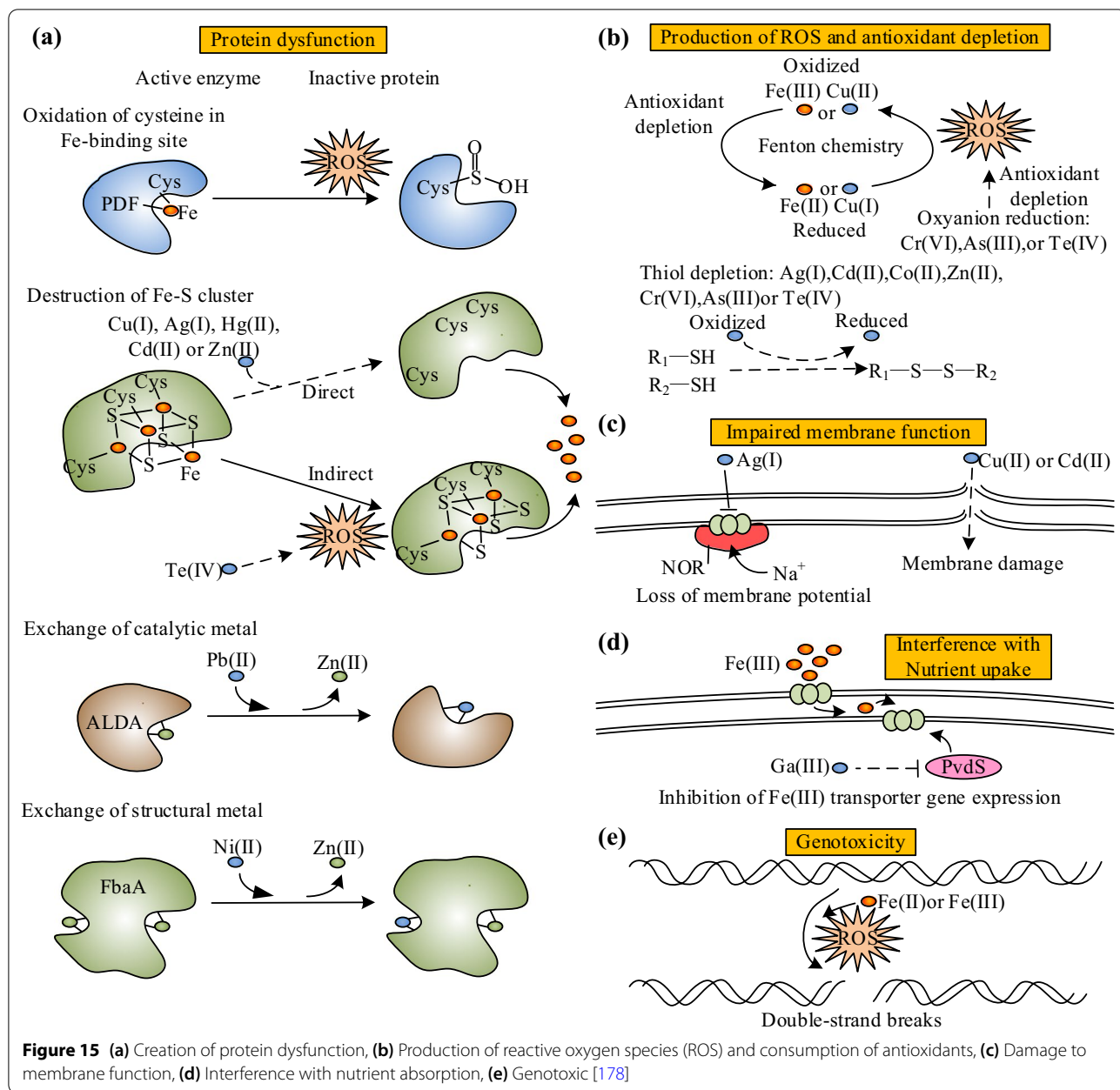


Table 6 Bactericidal properties of transition metal complex

Material	Atomic number	Zone of inhibition (mm)	Ref. No.
Mn	25	9.5	[185]
Fe	26	15–30	[186]
Co	27	20–34	[187]
Ni	28	10–40	[186]
Cu	29	7–36	[186]

from Table 6 as follows: as the atomic number of transition metals increases, the sterilization performance of the complexes improves to a certain extent.

Scholars found that the products after complexation of transition metals and bactericides could prolong the use time of bactericides and enhance the energy efficiency of sterilization. Furthermore, a large number of chips could be generated during metal processing, and the metal ions precipitated during the processing may enhance the sterilization ability of the complex.

5.3 Physical Sterilization Method

In addition to the study of new chemical bactericides, physical methods could be used to inactivate microorganisms in cutting fluid. Ozone, UV, and others have certain bactericidal effect in various fields.

5.3.1 Ultraviolet Ray

The wavelength of UV light is 10–400 nm, and its radiation could cause the connection between adjacent pyrimidine bases in DNA. This phenomenon inhibits its correct replication during cell division and affect the reproduction of microorganisms. As a rule of thumb, the mechanisms through which UV radiation could damage microorganisms are as follows: (i) the photo-induced reactions resulting from the direct absorption of UV photons by biopolymers, especially NAs and proteins, which are the basic constituents in common between bacteria and viruses [188, 189], and (ii) the photo-oxidation triggered by ROS generated after UV irradiation of exogenous and endogenous photosensitizers, i.e., powerful oxidant materials or photosensitive molecules other than NAs and proteins [190].

In addition, UV rays are almost non-hazardous, and they do not cause fire or toxic contact with workers; the effect of UV sterilization depends on the radiation power, radiation time and radiation area. Due to the low transparency of the cutting fluid, the penetration depth of UV rays is reduced, and the sterilization effect is greatly reduced. Microbes have the ability to repair themselves, which could repair the damage caused by radiation, further reducing the sterilization ability of UV light. Ensuring a higher power when the cutting fluid is sterilized by UV rays is necessary and the cutting fluid should be kept flowing continuously to achieve enhanced sterilization effect [191].

A notable detail that the inactivation of microorganisms is strictly dependent on the amount of radiation absorbed and capable of giving rise to detrimental effects. Accordingly, some parameters play a key role on the disinfection behavior, one above all is UV dose (referred to as fluence), generally expressed as the product of the UV light intensity (I) and the irradiation time (T_{irr}), where

UV dose is commonly expressed in $J/cm^2 = W \cdot s/cm^2$ [192].

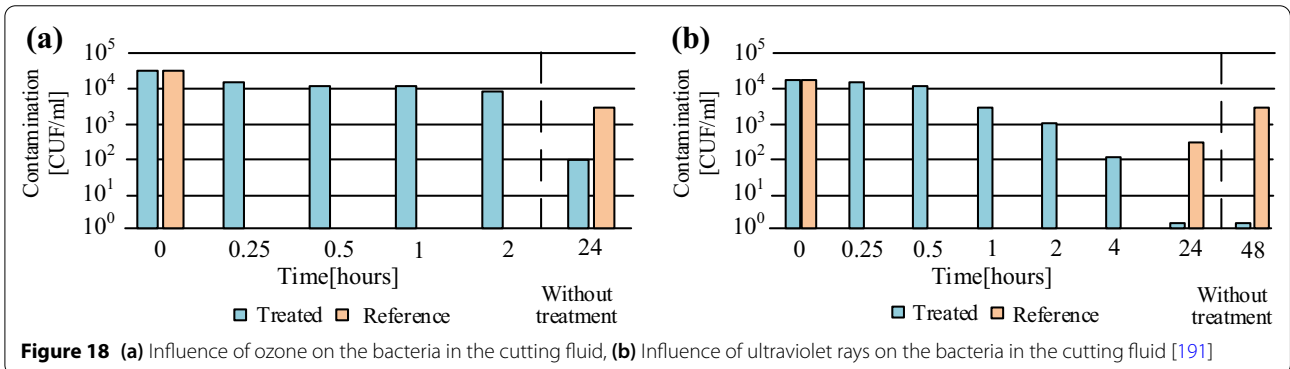
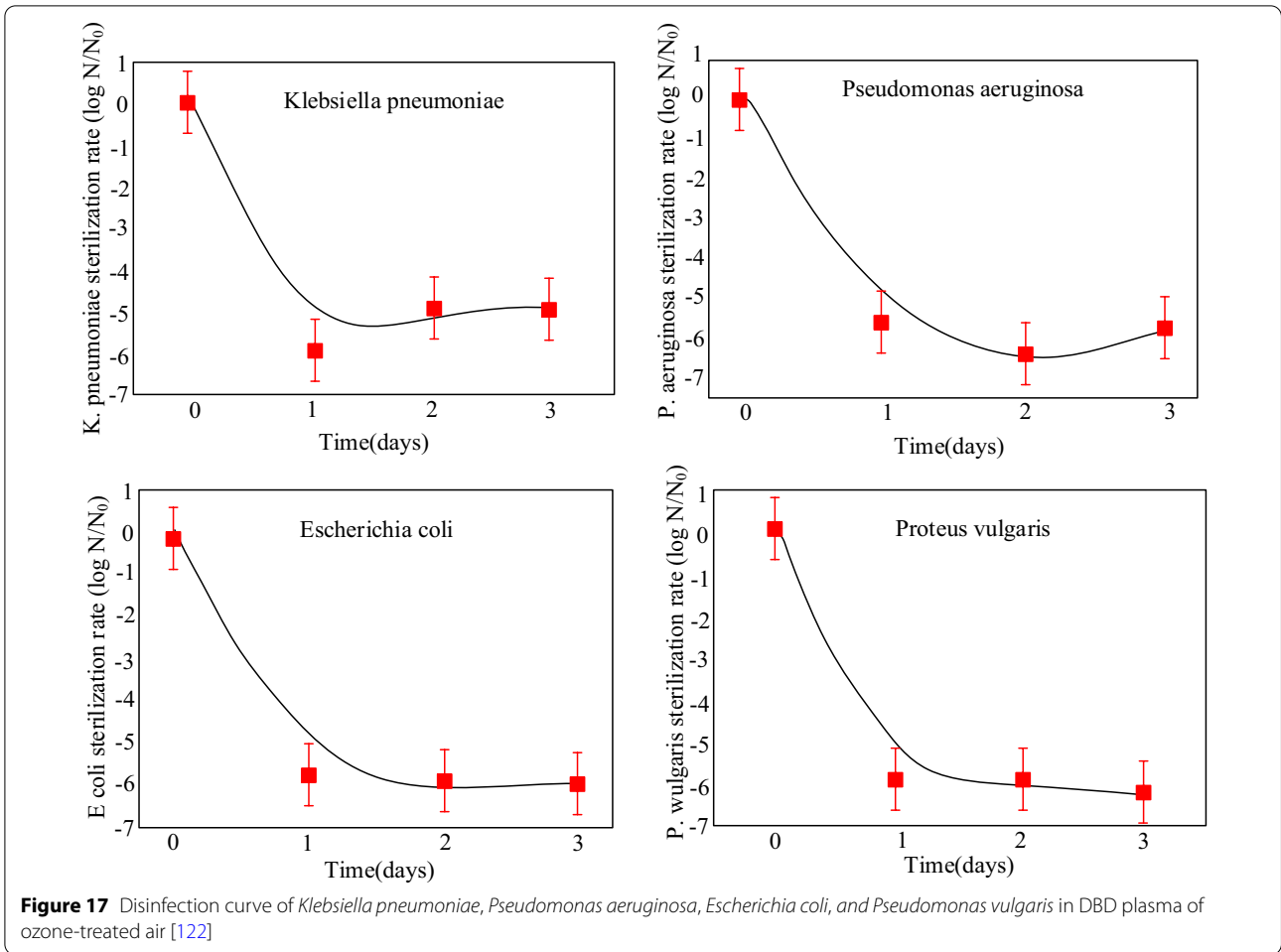
Souza used 16 caluv lamps for 24 h of treatment of cutting fluid and achieved an average reduction of 99.70% contamination of synthetic cutting fluid [193]. In addition, considering that the opacity of the cutting fluid weakens the transmission of UV light to a certain extent, Johnson et al. used a high-output UV lamp that could withstand harsh chemical environments for experiments. Enhanced results were achieved, and the UV bactericidal rate reached more than 99% [47]. Weigel's UV sterilization experiment found that *E. coli* cells were inactivated within 5–15 s, and fecal *E. coli* cells were inactivated within 30 s [194].

5.3.2 Ozone

Ozone is one of the most effective strong oxidants that could effectively inactivate microorganisms. In addition, it could rapidly decompose into oxygen molecules in water, and it does not form any secondary pollutants. Kristina et al. verified the sterilization ability of ozone through experiments. The initial bacterial concentration was 10^7 CFU/mL, and the microorganisms were completely eliminated 20 min later [48, 49]. Ma proposed an ozone treatment system using air DBD plasma to stably generate high concentration ozone and inject water-based cutting fluids. He used *Klebsiella pneumoniae*, *P. aeruginosa*, *E. coli*, and *P. vulgaris* for sterilization experiments and counted the microbial colonies in the treated water for 3 days, as shown in Figure 17. Experiments confirmed that the sterilization rate of water-based cutting fluids could reach 99.99%. The turbidity, pH value, and odor of water-based cutting fluids all improved. Among them, *K. pneumoniae* proliferated slightly after 2 days of sterilization, and *P. aeruginosa* proliferated slightly after 3 days of sterilization. Therefore, to maintain the effect of ozone treatment, Sukhwal Ma proposed a strategy of using an air DBD system to treat the cutting fluid every 3 days [122].

The vertical axis in Figure 17 is the logarithmic value of N/N_0 , where N_0 is the number of surviving control colonies in CFU/mL. The average control numbers were 8.2×10^6 , 7.0×10^6 , 2.4×10^6 , and 2.8×10^6 CFU/mL; the results showed that the values of $\log(N/N_0)$ were -6 , -5.6 , -5.9 , and -6.15 , respectively. This logarithmic scale indicated that more than 99.9% of bacteria were killed [122].

Nadine Madanchi developed an experimental cutting fluid circulation system and studied the inactivation effect of ozone, UV, and other sterilization methods on microorganisms in the cutting fluid under this system. The experimental results are shown in Figure 18 [191]. Both methods of sterilization were found to



have enhanced results. The effect of ozone on cutting fluid was not obvious within 2 h, but the microorganism decreased from 10^{4.5} CFU/mL to 10² CFU/mL after 24 h. Within 24 h, the sterilization effect of UV was remarkable, and almost no bacteria could be detected.

In addition, the experimental results demonstrated that the number of microorganisms in the cutting fluid without sterilization treatment was reduced to a certain extent. Therefore, the flow of cutting fluid also helps reduce the microbial population [191].

5.3.3 Fine Bubbles

Fine bubbles (defined as bubbles with a diameter below 100 μm , referred to as FB) could fulfill different functions depending on their gas composition, bubble size, and bubble density, such as the action of microbubble disruption for bactericidal and cleaning [195]. Bubbles with a diameter of 1–100 μm are called microbubbles (MBs), and bubbles with a diameter of less than 1 μm are called ultrafine bubbles (UFBs). Because UFB is small in size, it could stay in the liquid for a longer time, thus takes longer to function. Hiroko Yamada prepared UFBs with two gases (air and CO_2), and the bactericidal effect against *P. aeruginosa* (gram-negative bacteria) and *S. aureus* (gram-positive bacteria) was experimentally verified [50]. The experimental results found that the sterilization rate of CO_2 -UFB was 100% against *P. aeruginosa* and 0% against *S. aureus*. Fluorescence microscopic observation showed that the cause of *P. aeruginosa* cell death was cell wall damage, because the cell wall thickness was 6–10 nm for *P. aeruginosa* and 20–40 nm for *S. aureus*. In addition, the cell wall of Gram-positive bacteria is composed of multiple peptidoglycan layers. These peptidoglycan layers could reduce the internal pressure of bacteria and prevent cell rupture [50].

Table 7 summarizes the sterilization effects of different sterilization methods. Ozone and UV rays have better sterilization effects, while FB sterilization could only act on Gram-negative bacteria.

6 Comprehensive Evaluation of Sterilization Methods

On the basis of the above research status, a comprehensive comparative evaluation of traditional sterilization methods and physical sterilization, as well as nanomaterials and transition metal complexes was conducted in this paper. The evaluation indicators included sterilization performance, hazard, degradability, and economy, as shown in Table 8.

Different modes of sterilization were found to have their own advantages and disadvantages through the above multiple modes of sterilization. The sterilizing activity of each methods on different microorganisms

Table 7 Sterilization effect of physical sterilization methods

Method	MIC (mg/mL)	Colonies number (CFU/mL)	Percentage inhibition
O_3	<i>S. aureus</i> : 0.24; <i>E. coli</i> : 90	$10^{4.5}$ to 10^2	99.9%
UV		$10^{6.5}$ to 0	99.2%
Fine bubble			<i>P. Aeruginosa</i> : 100% <i>S. aureus</i> : 0%

Table 8 Comparison of various sterilization methods

Method	Performance	Harmfulness	Degradability	Economy
Traditional	***	***	*	**
Ozone	***	*	***	*
UV	***	*	***	*
Fine bubbles	**	*	***	*
Nanomaterials	**	*	**	**
Metal complex	***	*	**	***

Note: * Representative grade

also varies. For example, certain microorganisms could develop resistance to partial chemical bactericides and FB bactericidal method is more applicable to Gram-negative bacteria. Therefore, when a sterilization method could not achieve the expected effect, coupling multiple sterilization methods could be considered while ensuring the cost to extend the service life of cutting fluids.

7 Conclusions and Outlook

In this article, the biological stability of water-based cutting fluids and the sterilization principles and sterilization effects of various sterilization methods were reviewed. The main conclusions drawn are as follows.

- (1) The molecular structure in the water-soluble cutting fluid is easily decomposed by the invading microorganisms, leading to failure, a reduction in the life of the cutting fluid, and an increase in processing costs. Especially after the microorganisms gather to form a biofilm, the covered area could promote electrochemical conditions to form an electric current, which could corrode the metal and destroy the processing quality. Therefore, improving the biological stability of water-soluble cutting fluids is very important.
- (2) Traditional bactericides include borate and formaldehyde. Borate is used to change the permeability of the cell membrane to cause the bacteria to rupture and die. Formaldehyde mainly uses denaturation to change the protein structure and interact with NAs to inhibit bacterial reproduction. The main influencing factor of these two bactericidal effects is the concentration of the bactericide. When the concentration is 5%, it has a better antibacterial effect. However, these two substances are extremely harmful to human health.
- (3) Nanomaterials are a new type of sterilization method that has the characteristics of low toxicity

to the human body and strong sterilization performance. They have a strong application prospect. They could disturb the cell membrane potential and affect the integrity and permeability of the cell membrane, thereby triggering the leakage of intracellular material. The smaller particle size of the nano-bactericidal materials has stronger dispersibility, which could effectively improve the sterilization performance.

- (4) Transition metals have good biocompatibility, and they are easily degraded. The metal atoms in the center of the coordination compound have strong lipophilicity, which is conducive to allowing the complex to pass through the lipid layer of the microbial cell membrane. Then, it interferes with the genetic material in the nucleus. The higher the atomic number of the transition metal complexes is, the stronger the antibacterial properties. Meanwhile, the combination of the transition metal with the higher atomic number and the bactericidal compound could enhance the bacteriostatic ability of the compound. However, the underlying mechanism needs to be further explored.
- (5) Physical sterilization methods, such as ozone, UV rays, and FBs have the least harm to the human body; they could kill bacteria through their strong oxidizing properties, inhibition of DNA replication, and surface tension, respectively. The sterilization effect of this kind of sterilization method is better, but the economy is not high. Whether this kind of method could be applied to industrial production depends on the research of new low-cost realization methods.

In future research, preventing the proliferation of microorganisms in cutting fluid could also be considered from the following points.

- (1) Change the composition of additives in the cutting fluid. Most additives with emulsification, corrosion inhibition, and lubrication functions are straight-chain organic derivatives, which are easily decomposed by microorganisms. Branched alternatives, such as isostearic acid and polyester emulsifiers, could also be considered.
- (2) Develop a hybrid sterilization system to control the number of microorganisms and increase the killing rate of bacteria and the destruction rate of biofilm by using the method of combining biological sterilant and physical sterilization to extend the service life of cutting fluid.
- (3) Conduct frequent liquid monitoring to measure bacteria/fungus, free oil, pH, and concentration.

Establish and improve the database, respond to the monitoring data in a timely manner, and supplement the bactericide.

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Authors' contributions

CL was in charge of the whole trial; LT and YZ wrote the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare no competing financial interests.

Author Details

¹School of Mechanical and Automotive Engineering, Qingdao University of Technology, Qingdao 266520, China. ²Hanergy (Qingdao) Lubrication Technology Co., Ltd., Qingdao 266200, China. ³Nanjing Kerun Lubricants Co., Ltd., Nanjing 211106, China. ⁴Chengdu Tool Research Institute Co., Ltd, Chengdu 610500, China. ⁵School of Mechanical Engineering, Chongqing University, Chongqing 400044, China. ⁶Sichuan Future Aerospace Industry LLC, Shifang 618400, China. ⁷Shanghai Jinzhao Energy Saving Technology Co., Ltd., Shanghai 200436, China. ⁸Department of Sustainable and Renewable Energy Engineering, University of Sharjah, 27272 Sharjah, United Arab Emirates. ⁹Mechanical Engineering Department, Curtin University, 98009 Miri, Malaysia. ¹⁰College of Mechanical and Electrical Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China. ¹¹Mechanical Engineering Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia. ¹²Department of Mechanical Engineering, IK Gujral Punjab Technical University, Kapurthala 144603, Punjab, India.

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