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Biofouling control method based on quaternary ammonium compounds

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ABSTRACT

In the pretreatment process of seawater intaking, the prevention and treatment of biofouling is very important. Prior industry surveys have estimated that condenser biofouling, on average, accounts for a 3% loss in generating unit availability, of which 40% can be attributed to biological fouling [1]. Among several control methods, adding chemical reagent is the most popular approach. Quaternary ammonium compound (QAC) biocides are kinds of important nonoxidizing biocides, which have developed through generation products. These are classified into three types as single-chain QAC, double-chain QAC, and polymeric QAC, based on their structural characteristics. In recent years, the application field of QAC has gradually extended from killing bacteria to preventing and controlling mollusk infestations [2]. In this article, we try to briefly introduce the research progress of QAC and the action mechanism by the structures. We hope to provide a new way to solve such biofouling problem for the related researchers.

Keywords: Quaternary ammonium compounds; Biocide; Biofouling defense

1. Introduction

Quaternary ammonium compounds (QACs) are the major class of cationic surfactants used as the biocides. Because Domagk discovered the antimicrobial property of benzalkonium chlorides in 1935, generations of QAC with various structures have been explored. A survey on approximate 500 US Environmental Protection Agency registered disinfectant products showed that QACs were the most popular biocides being applied in 57.8% of the formulation [3].

Single-chain QACs are molecules with at least one long hydrophobic hydrocarbon chain linked to a positively charged nitrogen atom. The other alkyl groups are mostly short-chain substituent such as methyl or benzyl groups. The counter ions can be either inorganic or organic. It was reported that long-chain QAC with 8–18 carbon atoms possessed germicidal activity when at least one of the four Rs was a plain or substituted aliphatic group [4] (Table 1). The QAC with chain lengths of 12–14 alkyls would get the optimal activity against Gram-postive bacteria and yeast; however, compounds with chain lengths lesser than 4 or greater than 18 were virtually inactive [5].

Double QACs, also called gemini surfactants, belong to a new class of very effective surfactants. Gemini surfactants possess at least two hydrophobic hydrocarbon chains and two hydrophilic quaternary ammonium groups, which are connected by a spacer. From a structural point of view, a spacer can be rigid (aromatic or unsaturated linear hydrocarbons) or flexible (polymethylene chain). The neutral charge of the molecule is retained by the presence of counterions, which are usually halide anions. The gemini compounds also exhibit a very high antimicrobial activity against bacteria, viruses, moulds, and yeasts [6].

Polymeric materials containing QACs have been extensively studied and applied to a variety of antimicrobial-relevant areas. Usually, these kinds of materials were made from modification of quaterisation fatty alkyl or from a polymer of a cationic monomer containing double bonds.

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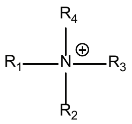
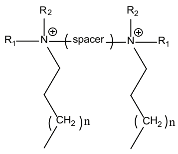
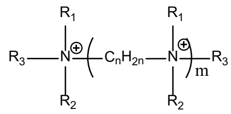
Table 1
The general structure of quaternary ammonium compounds (QACs)

Structure of single-chain QAC	Structure of double-chain QAC	Structure of polymeric QAC
		
R_1, R_2, R_3, R_4 = $–CH_3$,$–C_nH_{2n+1}$ (n = 8–18), $–CH_2C_6H_5$	R_1, R_2 = $–CH_3$,$–C_nH_{2n+1}$, (n = 5–18), $–CH_2C_6H_5$	R_1, R_2, and R_3 are long carbon chain (or containing aryl substituent), $m > 2$

These polymers containing covalently bonded antimicrobial moieties avoid the problem of the permeation of low molecular weight biocides from polymer matrices [7]. In addition, antimicrobial polymers posses chemical stability and nonvolatility and present a long-term activity [8].

In this article, we will briefly introduce the research progress of QAC and try to describe the structure–function relationship of these compounds. We hope to provide a new way to solve such biofouling problem for the related researchers.

2. Progress in the research on the antibiotics of QACs

2.1. Development of single-chain QAC

As the name suggests, a single-chain QAC is a QAC containing only one long chain. It is the basis for the development of such surfactant. After a long time of development, it still occupies an important position in the market.

Zhang and Gao [9] studied the algae removal effect by dodecyl dimethyl benzyl ammonium bromide, dodecyl dimethyl benzyl ammonium chloride, and tetradecyl benzyl dimethyl ammonium chloride to the direct cooling water discharge of a petrochemical enterprise. When the mass concentration of single-chain quaternary ammonium salt was more than 25 mg/L, the algae removal rate was above 90%, and the effluent quality achieved the requirements of industrial water treatment.

Growth inhibition of cetyltrimethyl ammonium chloride (CTAC) on *Chlorella vulgaris* was investigated by Xu et al. [10]. The results showed that the growth inhibition by CTAC was enhanced with its concentration increasing from 0.1 to 1 mg/L, and 96 h-EC_{50} of CTAC was 0.18 mg/L [10].

The research results of Hong et al. [11] showed that bromogeramine could kill and control *Prorocentrum micans*. Glutaraldehyde and bromogeramine were studied separately by testing the algaecide number reduction percentage acting alone and in combination with different concentrations. It could inhibit the growth in the concentration of 0.1 mg/L; when the concentration got 0.15 mg/L, the extinction rate could be up to 90% [11].

In addition to sterilization, the single-chain quaternary amines were also the most widely used compounds to control macrobiofouling, which were firstly applied and registered in the US for mollusk control in 1986. One reason for their success was the remarkable selectivity of the target organism.

Spectrus CT1300 is a mixture of single-chain QACs, which is completely odorless. It was tested once on adult *L. fortune* at Embalse Rio Tercero Nuclear Power Plant (Argentina) with a nominal concentration of 2.5 ppm [12]. The results showed that in the biobox treated with Spectrus CT1300, mortalities increased with time: 63% of the mussels were killed in 24 h, 94% in 48 h, and 99% in 72 h. After 72 h, there was zero mortality in the control and only 1.2% mortality in the biobox treated with chlorine. After considering the seawater macrofouling character, biocide performance, and cost control issue, Zhuhai Power Plant [13] and Guangdong Red Bay Power Generation Company [14] also adopted Spectrus CT1300 as their major method to control biofouling infestations.

Many QACs showed a low biodegradability. For example, dioctadecyldimethylammonium chloride, the major component of the commercial product ditallowdimethylammonium chloride (DTDMAC), was mineralized very slowly, and its ultimate biodegradation was lower than 5% [15]. Actually, the degradation process is very complex and strongly depends on the structure of the compounds, adsorption–desorption processes on sludge, types of microorganism consortia, and the presence of anions. Alkylammonium surfactants with biological motifs, like amide, peptides, or carbohydrates are much better degraded [16].

N-alkyl dimethylbenzyl ammonium chloride (ADBAC) is a familiar material which has been used in a broad spectrum of household and industrial applications for more than 50 years, with current annual US consumption estimated at 30–40 million pounds [17]. The structure of ADBAC is shown in Fig. 1, alkyl chain = 8–16 carbon. Today, the largest antimicrobial usage for ADBAC is swimming pool algaecide. Effective dosages in swimming pools are the same as those required for mollusk control, 1–3 ppm. It is also effective against Asiatic clams, as well as saltwater mollusks, as shown in Fig. 2.

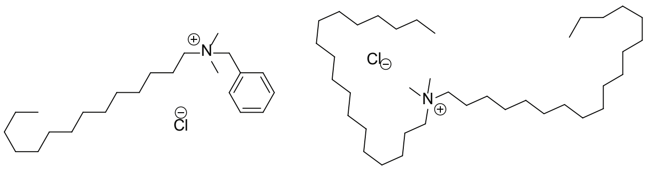
Patrauchan and Oriel [18] investigated *Aeromonas hydrophila* sp. K and found that these microorganisms were able to degrade xenobiotics, such as ADBAC. However, because of the toxicity of these compounds, the biodegradation process of ADBAC was not complete, and its efficacy depended on the initial surfactant concentration [18].

2.2. Research on double-chain QAC

As time goes on, some shortcomings of the single-chain quaternary ammonium biocide are gradually emerging, such as drug resistance, foam producing, and so on. Therefore, double-chain quaternary ammonium biocide has been exploited these years. Double-chain QACs are distinguished from conventional surfactants by two cationic head groups and two alkyl chains, which have been studied by many chemists worldwide [19,20]. These compounds possess a unique structure, a greater surface activity, and more excellent antimicrobial potency than conventional surfactants. Many synthesized surfactants are composed of various hydrophilic groups and spacer chains; their hydrophilic groups are ionic polar head and a nonionic polar head; and their spacer chains are polar chain and a nonpolar chain [21].

A dissymmetric double-chain quaternary ammonium salt was synthesized by one-step process from C–12 alkyl tertiary amine and epichlorohydrin [22]. The results showed that the sterilization rate of heterotrophic bacteria was 90.43% in 8 h and over 80% in 16 h, respectively. To the iron bacteria, the sterilization rate was easily up to 96.79% in 4 h and was maintained between 95% and 100% within 44 h. The bactericidal capability was superior to the conventional bactericide 1227.

Mao et al. [23] synthesized a series of quaternary ammonium gemini surfactants *n*–2–*n* (*n* = 8, 10, 12, 14), by



ADBAC DTDMAC

Fig. 1. Structures of ADBAC and DTDMAC.

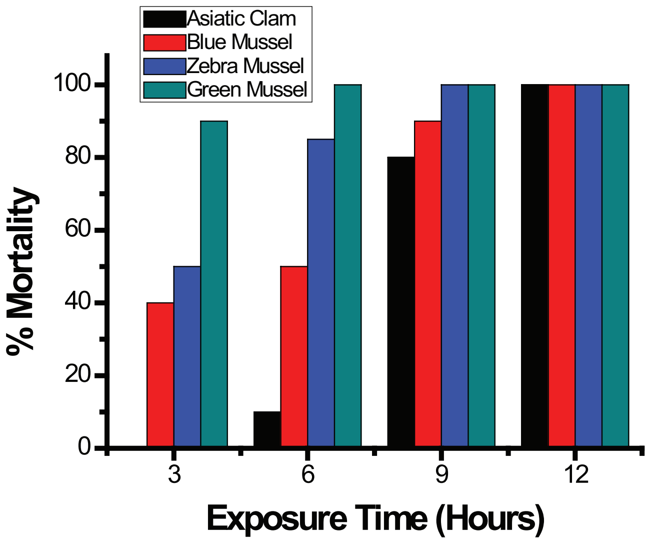


Fig. 2. Dose-response data for 2 ppm ADBAC against mollusks at 25°C.

quaterisation of *N′N′N′N′*-tetramethyl ethylene diamine and bromo alkane. The antibacterial abilities of *n*–2–*n* were investigated on sulfate-reducing bacteria (SRB), ferrobacillus (FB), and total growth bacteria (TGB) that commonly present in oilfield brine. The results showed that *n*–2–*n* exhibited superior biocide properties, and the antibacterial ability boosted with the increasing of chain length. Concentration of 20 mg/L 12–2–12 or 14–2–14 resulted in 99% mortality of SRB, FR, and TGB.

Novel biocides of bis-QACs consisting of two identical alkylpyridium rings and a bridge structure which linked the two parts were synthesized by Huang et al. [24]. These compounds (Fig. 3) with two hydrophilic groups, two hydrophobic groups, and two ammonium in each molecule had excellent surface activity and antimicrobial activity.

Taking DOCBP as an example, the compounds had excellent bactericidal effect against *Staphylococcus aureus*, *Micrococcus lysodeikticus*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Escherichia coli*, *Proteus vulgar*, and other bacteria. The corresponding minimum inhibitory concentration (MIC) was 0.5–25 ppm. It also had a good inhibitory performance on moulds, such as *Aspergillus niger* and *Penicillium citrinum* with an MIC of 100 ppm. The overall bactericidal effect was severalfold even a few times better than the corresponding single QACs.

A dissymmetric bis-QAC surfactant was synthesized by employing trimethylamine hydrochloride, epichlorohydrin, and dimethyldodecylamine (Fig. 4). The bactericidal performance was studied, and the results showed that the bactericidal effect could be up to 99% at 25 mg/L. Its performance was much better than the glutaraldehyde [25].

Zhao et al. [26] reported a cationic dimeric amphiphile 12–8–12 and determined its antibacterial activity by the result of β-galactosidase activity and the SEM image of *E. coli*. The result showed that this kind of compound could disrupt the cell membrane of *E. coli* leading to the releasing of intracellular contents and the death of the bacterial cells, which was better than the corresponding monomeric compound [26]. The MIC of 12–8–12 was 0.4 mg/L, which was about 1/20 of corresponding monomeric compound.

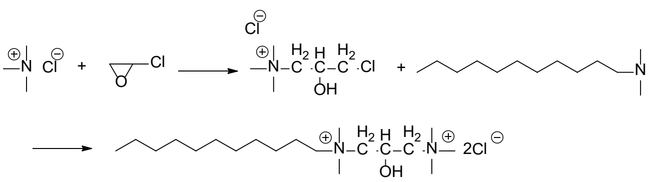
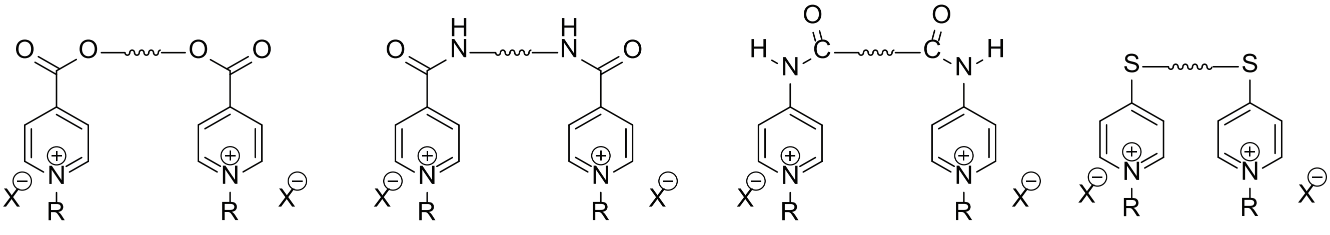


Fig. 4. The synthetic route of a new double-chain QAC.



DOCBP BCAP DCABP DTBP

Fig. 3. Some new structures of double-chain QAC.

The ever-widening application of gemini surfactants increases the possibility of their presence in surface water and sediments; however, few papers investigate the biodegradability of gemini surfactants.

Banno et al. [27] studied the biodegradation of conventional gemini cationic surfactants and surfactants with carbonate linkages introduced into the hydrophobic moiety in the spacer or in both the hydrophobic and spacer moieties. The carbonate linkage in the linker moiety was gradually hydrolyzed in water and only 18% remained after 9 h of reaction, while 97% of the carbonate linkage in the hydrophobic moiety remained after the same period. These results indicated that the carbonate linkage in the hydrophobic moiety was more stable against hydrolysis than the carbonate linkage in the linker moiety [27].

Tehrani-Bagha and Holmberg [28] prepared decyl and dodecyl homologs of gemini ester quats and betaine esters with different numbers of methylene groups in the spacer. They also synthesized corresponding monomeric compounds. They found that the monomeric surfactants were rapidly degraded (above 80% at Day 28), while the gemini surfactants were more resistant to biodegradation. Dodecyl betainate and dodecyl ester quats required 42 d to reach more than 60% biodegradation, while the decyl homologs of ester quats did not exceed 45% even after 55 d [28].

Thus, the gemini surfactants that have been studied could not be classified as readily biodegradable. The poor biodegradability of those gemini surfactants is most likely due to the slow degradation of the dicationic species. These species, which were synthesized and tested for biodegradation, degraded very slowly (less than 20% after 28 d), indicating that they were resistant to biodegradation [28,29].

2.3. Polymer QAC biocide and its application

The cellular membranes of most bacteria are negatively charged and have proven to be the target site of cationic biocides [30]. The antibacterial mechanism of biocidal QAC, a class of membrane-active cationic biocides, has been proposed to be penetration into the cell wall and destructive interaction with the cytoplasmic membrane, followed by the leakage of intracellular components and consequent cell death [31]. Compared with low molecular weight QAC, polymeric QAC has higher positive charge density which promotes initial adsorption onto the negatively charged bacterial surfaces and disruption of cellular membranes, resulting in significantly enhanced antibacterial activity [32].

It has been reported that a long alkyl-chain substituent, for example, at least eight carbons, usually exhibit higher biocidal activity [33]. Dizman et al. [34] synthesized a methacrylate monomer containing pendant QAC based on 1,4-diazabicyclo[2.2.2]octane, which contained either a butyl or hexyl group. Although the monomers did not show any anitimicrobial properties, the corresponding homopolymers were effectively bactericidal against *S. aureus* and *E. coli*. Their activities were found to be dependent on the length of the hydrophobic segments, and the polymer with hexyl group was more effective than that with butyl groups. The MIC values of the polymers with butyl and hexyl hydrocarbon chains against *S. aureus and E. coli* were found to be 250 and 62.5 mg/mL, respectively.

Pera [35] prepared a series of polymeric quaternary ammonium compositions by the reaction of epichlorohydrin with mixtures of dimethylamine for the control of microorganisms, for example, bacteria and algae in industrial and commercial installations employing water. The bactericides of the invention were substantially nonfoaming and nonirritating to humans, animals, and fowl.

In 2006, Dizman et al. [36] prepared three water-soluble methacrylate-based homopolymers Poly(α-chlorovalerylethylmethyl acrylate) with pendant QAC functionality, where 12-carbon, 14-carbon, and 16-carbon alkyl chains were appended to the QAC. All these three polymers were active toward *S. aureus* and *E. coli*, with activities ranging from 32 to 256 mg/mL [36]. Polydiallyldimethyl ammonium chloride was originally produced in 1957 and structurally similar to a number of poly-quaternium structures. This water-soluble polymer beared a pyrrolidinium group and has been found to have an extended use in wastewater treatment and some other applications [37] (Fig. 5).

Kenawy et al. [38] developed two kinds of cross-linked copolymers through copolymerization of vinylbenzyl chloride with 2-chloroethyl vinyl ether or methylmethacrylate using divinylbenzyl chloride as the crosslinker, followed by quaternization with tertiary amines. The antimicrobial properties of prepared copolymers were studied using a cut plug method against bacteria and fungi [38]. Concentration of 20 mg/mL of these polymers could kill 100% of *Candida albicans*.

BULAB 6002 (Poly[oxyethylene{dimethyliminio}ethylene{dimethyliminio}ethylene dichloride]) is a liquid cationic poly QAC used for algae control in swimming pools and as a microbicide microorganisms defense in the industrial water systems. It is also considered to be an effective molluscicide. Darrigran et al. [39] tested the effectiveness of BULAB 6002 on both juvenile and adult golden mussels. Cumulative mortality was assessed in six experiments conducted with different size classes of mussels and different concentrations of the product (8, 12, and 20 mg/L of active substance). The result showed that after exposure in 20 mg/L Bulab 6002 for 144 h, the mortality of adult golden mussels was 100%.

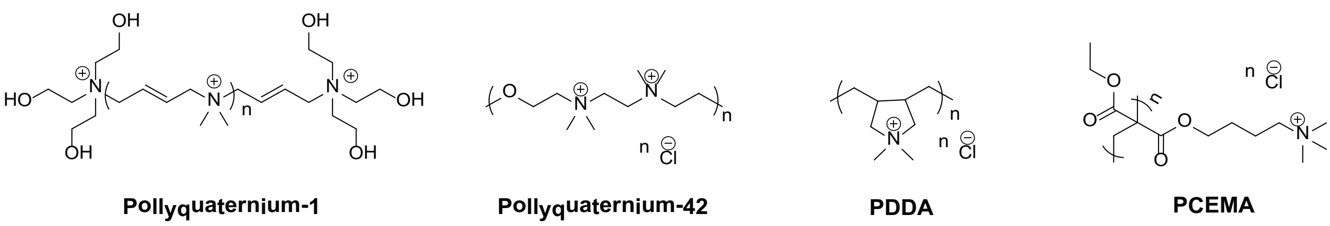


Fig. 5. Commercialized antimicrobial quaternary ammonium polymers.

The polymeric cations that have been developed are relatively poorly degradable so far, especially for poly-ammoniums, most of which are nondegradable. However, appropriate chemical modification with biological motifs, such as peptides or ester, could make it degrade more. Biodegradable poly(ε-caprolactone) (PCL) with antimicrobial property [40] was prepared by grafting alkyne-containing QAC to presynthesized azide-containing PCL (Fig. 6). Accompanying the biodegradability, a biocidal effect of the QAC-modified PCL was observed, which was analyzed via the shaking-flask test against *E. coli*. In 10 mL of the bacterial solution, 0.163 mmol of PCL killed all the bacteria within 1 h, in contrast to 0.175 mmol of corresponding monomeric ammonium was unable to kill bacteria within 2 h, although the monomeric one was soluble in water in contrast to the polymeric counterpart.

3. The action mechanism of QAC against microorganisms

Although there are differences in the structure of QACs in different generations, the ways they work are usually similar. Benefiting from the rapid development of characterization technology, various advanced technologies [41,42] have been applied to investigate the action mode. These studies provide intuitive and persuasive evidence for supporting the hypothesis about the antimicrobial mechanism of cationic biocides. At the molecular level, a model lipid bilayer membrane has been employed to simulate the permeability barrier of cellular membrane for understanding the interaction between cationic biocides and bacterial membrane [43]. The electrostatic interactions between the cationic polymers and the lipid head groups result in the formation of interfacial complexes within the outer leaflet. The interaction also induces flip-flop of anionic lipid molecules from the inside to the outside leaflet, followed by significant distortions and phase separation of the phospholipid bilayer [44]. In general, the following series of events involved in the action of QAC against microorganisms: (i) QAC adsorption to and penetration of the cell wall; (ii) reaction with the cytoplasmic membrane (lipid or protein), followed by membrane disorganization; (iii) leakage of intracellular lower weight material; (iv) degradation of proteins and nucleic acids; and (v) cell wall lysis caused by autolytic enzymes [45,46].

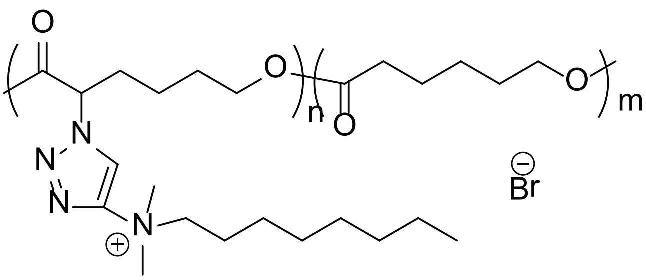


Fig. 6. Biodegradable antimicrobial poly(ε-caprolactone).

4. The recommendations and conclusions

For different objects, such as bacteria, algae, shellfish, etc., the dosage of QACs is not the same. According to the active ingredient content and water quality, the general dosage of QAC was from decimal to tens ppm. Considering the actual needs, some factories also choose a mix method of QAC with oxidized biocide dosing. Zhuhai Power Plant in China was the first one that used Spectrus CT1300 in circulating water system for the marine pollution control. The actual operating results proved that from the system operation, maintenance costs, and other aspects of the economic benefits, the use of Spectrus CT1300 could save 10 million Yuan than the use of chlorine [47]. The Spectrus CT1300 was an environment friendly, safe and reliable product, and easy to use. It had a remarkable effect on removing shellfish mollusks, and the utilization of the compound was a feasible and effective way to control marine biological pollution.

QAC biocide had well effect on many biofouling defenses. It has been widely used in many fields, including water treatment, and made a lot of new progresses recently. However, the correlation between the concentration and duration and the correlation between molecular weight and killing performance are still not clear. In addition to the three generation of compounds above, in many cases, it is difficult to adjust the functional series of quaternary ammonium salts through structural design, and the mixed quaternary ammonium biocide could exert its efficacy. We believe that, in the future, QACs would still play an important role in the global water treatment market and would continue to develop in an environmentally friendly way.

Acknowledgments

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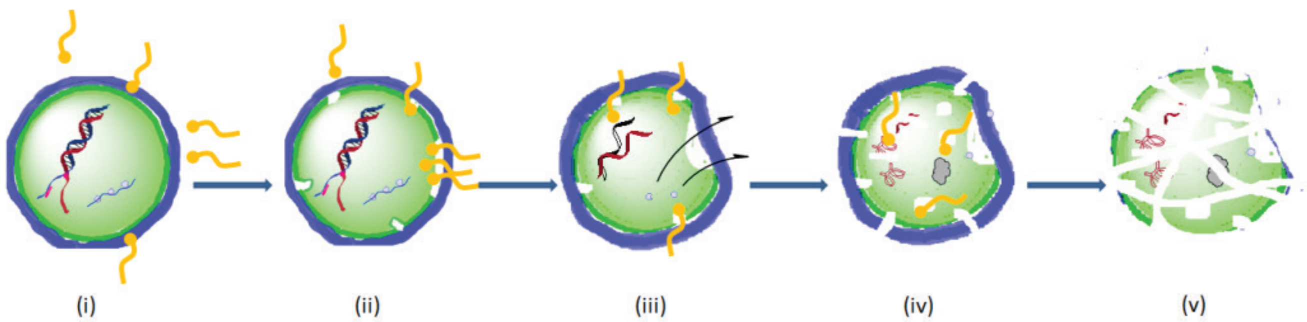

Fig. 7. The schematic of the QAC action mechanism.

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