



What choice do you make for sustainable QACs; DDAC or ADBAC?

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Abstract

QACs are cationic surfactants (surface active agents) and well-known biocidal agents. As an algae remover, they clean the algae from surfaces (detach) and restrict their growth (inhibit/kill). QACs interacts with negative charges on the cell membrane of microorganisms.

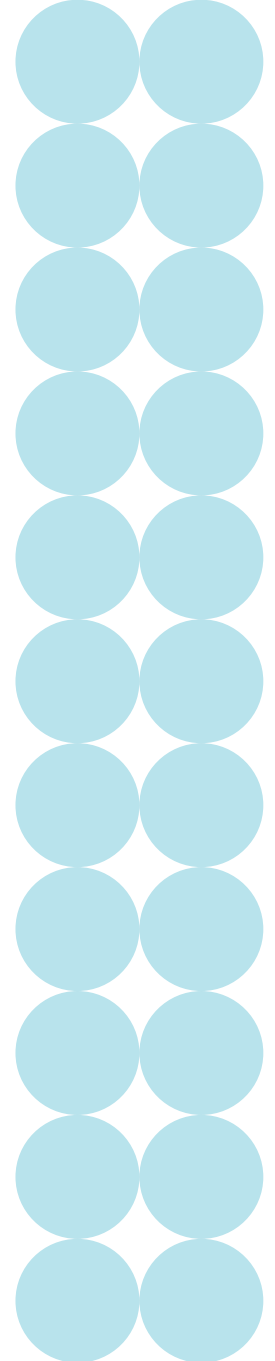
The DDAC molecule, having two alkyl chains destabilizes the phospholipids cell membrane more efficiently than ADBAC. Under 'dirty conditions' meaning surfaces where high organic matter (debris, soil, plant remains and animal excrement) is present, ADBAC is less effective than DDAC. Better tolerance and efficacy of DDAC are even more important in "green remover" applications where product (RTU or diluted on site with tap water with varying hardness) is applied directly to dirty surfaces. Also, because efficacy of DDAC is relatively higher than ADBAC against bacteria, mold, and algae, a reduced amount is needed for similar level of cleaning and antimicrobial efficacy. This can help save on use, shipping, carbon footprint and most importantly result in a lower amount of QACs discharged into the environment during use.

General introduction to quaternary ammonium compounds (QACs)

Quaternary ammonium compounds or QACs (sometimes referred to as quats), are a diverse group of cationic surfactants normally used for routine cleaning and disinfection of noncritical surfaces. QACs are among the most widely used classes of biocides, disinfectants, antimicrobials, and cleaners (Gerba, 2015). Due to their biocidal properties against bacteria, fungi, and viruses, QACs are used in household, food-processing, agriculture, and clinical settings to control the spread of environmentally transmitted pathogens (Merchel Piovesan Pereira & Tagkopoulos, 2019). QACs are membrane-active agents that interact with the cytoplasmic membrane in bacteria as well as the plasma membrane in yeast. Due to their hydrophobic activity, QACs are effective against lipid-containing viruses. They are also effective against both enveloped and non-enveloped viruses. QACs also interact with intracellular targets and bind to DNA (Zinchenko, Sergejev, Yamabe, Murata, & Yoshikawa, 2004). Generally, QACs are considered to be low level disinfectants. QACs are being increasingly included into contemporary products, which are utilized orally, like mouthwash, applied to the skin or eyes or administered as a nasal spray (Baudouin et al., 2010). QACs are often used in shampoos and laundry products to neutralize negative static charges and in cosmetics to preserve products from microbial contamination (Gao, 2007). Benzalkonium chlorides (BKC)s have often been applied for surface disinfection and hand hygiene in high concentrations which may be in some cases up to 80% (Liao et al. 2023). There is an extensive list of products available in the market used as green removers (remove algae from pavement, patios, deck, and roof) that are formulated with QACs.

The antimicrobial spectrum of most QACs is generally limited. Gram-negative bacteria are generally less susceptible than Gram-positive bacteria to QACs due to their outer membrane, which can make it somewhat more difficult for biocides to reach their target site (cytoplasmic membrane) (McDonnell & Russell, 1999; Denyer & Maillard, 2002). The challenge of

the limited efficacy of QACs against gram-negative bacteria has been progressively addressed and enhanced across the generations, from 1st to 5th generation QACs, each offering improved composition and performance (refer to table 1). Generations of QAC's represent how they evolved since 1935 when Domagk showed that improved germicidal activity could be achieved when a large aliphatic group was attached to the quaternary nitrogen atom. Alkyl dimethyl benzyl ammonium chlorides (ADBAC) were subsequently developed and referred to as "first generation" QACs. Since then, different QACs were made and mixed together that established different generations of QACs. Compared to 1st, 2nd, 3rd generation (for example C₁₂-C₁₆ ADBAC, C₁₂-C₁₄ ADEBAC and combination of these two), generation 4th and 5th (for example C₁₀-C₁₀ DDAC, C₈-C₁₀ DDAC) are typically more germicidal, less foaming, more tolerant of organic loads and anionic soaps and detergents. The effectiveness of QACs is affected by their structure. Among mono-alkyl QACs (ADBAC), chain lengths from C₁₂ to C₁₆ have greater inhibitory ability (Gerba, 2015). Double alkyl chained QACs (DDAC) are



better at killing Gram-negative bacteria (Jennings et al., 2015). In the following experiment, efficacy against Gram-negative bacteria and Gram-positive bacteria for Dialkyl QACs and mono-alkyl QACs were evaluated in a disinfectant cleaner formulation under simulated practical used conditions (Phase 2 Step 2 test). It was observed that C₁₀-C₁₀ DDAC (Dialkyl QAC) outperformed C₁₂-C₁₆ ADBAC (mono-alkyl QAC) by 0.5 and 1 log reduction in carrier test as per EN 13697 (phase 2 step 2) against *Pseudomonas aeruginosa* (Gram-negative bacteria) and *Staphylococcus aureus* (Gram-positive

bacteria) respectively (refer to fig 1). The disinfectant cleaner concentrate in the study was formulated with 6% active ingredient level for each QACs and the dilution of 0.25% of this formulation was used for the test delivering 0.015% each QAC in the test coupon. The test was performed under dirty conditions (3.0 g/l albumin) specified in the test standard.

Some products based on C₁₀-C₁₀ DDAC, C₈ C₁₀ DDAC may have a bacteriostatic residual effect, keeping surfaces bacteriostatic for a brief time.

Fig 1. Efficacy of QACs (C₁₀-C₁₀ DDAC and C₁₂-C₁₆ ADBAC) in disinfectant cleaner formulation on surface test (P2S2). A 0.015% active ingredient was evaluated as per EN 13697 standard under dirty conditions

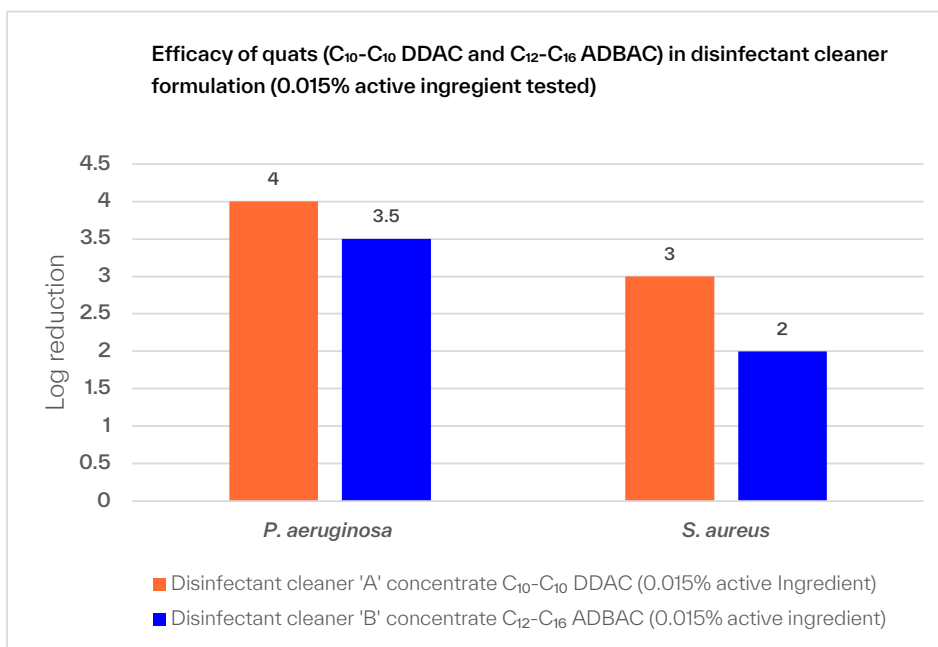
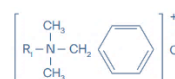
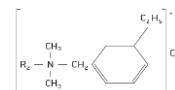
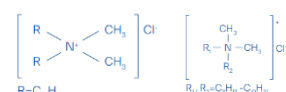
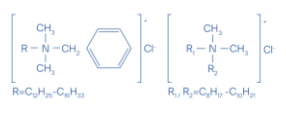


Table 1. Different generation of QACs

Generations	Active ingredient	Structure and example
1 st generation	ADBAC: Alkyl (C ₁₂₋₁₆) dimethyl benzyl ammonium chloride Benzalkonium chloride (BKC); [CAS Number 68424-85-1]	 Barquat® CB, DM, MB, BAC, MS, LB series R ₁ =C ₁₂ -C ₁₄
2 nd generation	ADEBAC: Alkyl (C ₁₂ -C ₁₄) dimethyl(ethylbenzyl)ammonium chloride [CAS Number 85409-23-0]	 No commercial product R ₂ =C ₁₂ -C ₁₄
3 rd generation	ADBAC + ADEBAC	Barquat® 4250Z / 4280Z
4 th generation	DDAC = Didecyl dimethyl ammonium chloride (C ₁₀ -C ₁₀ DDAC) [CAS Number 7173-51-5] DDAC = Didecyl dimethyl ammonium chloride (C ₈ -C ₁₀ DDAC) [CAS Number 68424-95-3]	 Bardac® 22 / 2240 / 2270
5 th generation	DDAC + ADBAC	 Bardac® 205M / 208M, Bardac® 114

Mode of action of QACs

QAC's mode of action is based on the interaction between the positively charged quaternary nitrogen with the head groups of the acidic phospholipids of the membrane and the negatively charged structural bacterial proteins (Maillard, 2002, Gilbert & Moore, 2005). The ionic interaction between QACs and the bacteria cell membrane destabilises the cell membrane, causing leakage of intracellular low-molecular-weight material, proteins, and nucleic acids, resulting in rapid cell lysis (Chapman, 2003). Thus, QACs function by irreversibly binding to the negatively charged phospholipids in bacterial cell membranes and denaturing membrane proteins impairing permeability. The structure of QACs, (C-chain length, number of Alkyl chain attached) determine its interaction with membranes and its efficacy. The better the interaction between the alkyl chains of QACs and the phospholipid membrane of microorganisms, the higher the efficacy.

Efficacy of QACs: DDAC outperformed ADBAC at 2 to 7 times lower concentrations

Efficacy data for C₁₀-C₁₀DDAC or C₈-C₁₀ DDAC against bacteria in quantitative suspension tests as per EN methods are mentioned in table 2. The data indicate C₁₀-C₁₀ DDAC is performing at lower doses compared to C₁₂-C₁₆ ADBAC under same conditions. It has been observed that C₁₀-C₁₀ DDAC was found to be efficacious at 2-3.5 times lower concentration in comparison to C₁₂-C₁₆ ADBAC under the same organic load and within the same contact time against bacteria as per EN 1276 and EN 1650 norms (refer to fig 2). It was also observed that C₈-C₁₀ DDAC (another type of dialkyl quat) passed the same test at 7.3 times lower concentrations compared to C₁₂-C₁₆ ADBAC against bacteria in clean condition (refer to fig 2). This significant difference in dose requirement for DDAC compared to ADBAC can help reduce the overall disinfection cost at the end-user level if DDAC QACs are opted for disinfectant formulations.

Table 2. Efficacy of QACs tested as per EN 1276 and EN 1650 under clean and dirty conditions.

Organism evaluated	EN test method	Active ingredient	Contact time	Soiling conditions	Active substance pass level (PPM)
Bacteria <i>Pseudomonas aeruginosa</i> , <i>Staphylococcus aureus</i>	EN 1276	DDAC (C ₈ -C ₁₀)	5 min	Clean	240
		DDAC (C ₁₀ -C ₁₀)	5 min	Clean	500
	≥5 log reduction required	DDAC (C ₁₀ -C ₁₀)	5 min	Dirty	1000
				Clean	1750
		ADBAC (C ₁₂ -C ₁₆)	5 min	Dirty	2000

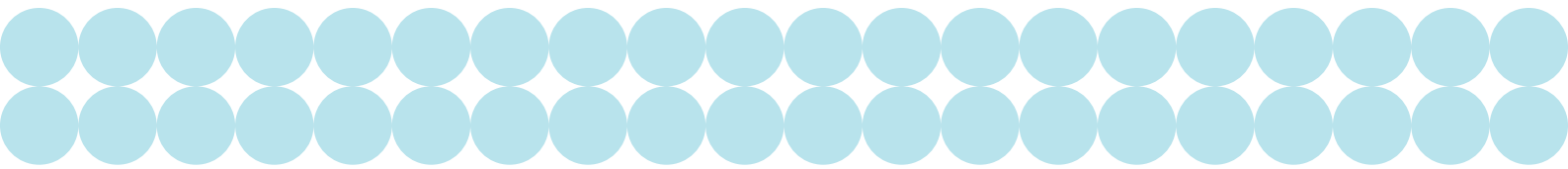
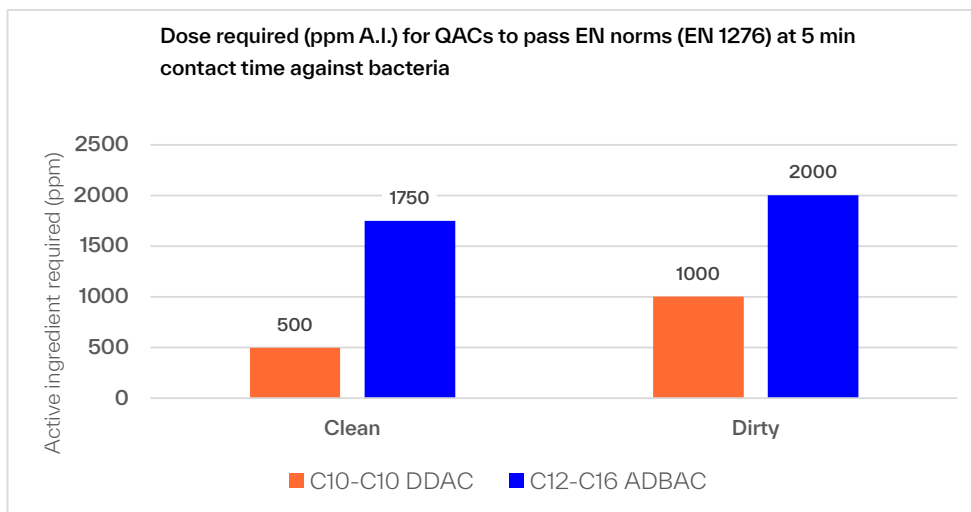


Fig 2. Graphical representation of table 2 to depict the pass concentration requirement of ADBAC Vs DDAC as per EN 1276 and EN 1650 in I&I clean and dirty conditions against bacteria

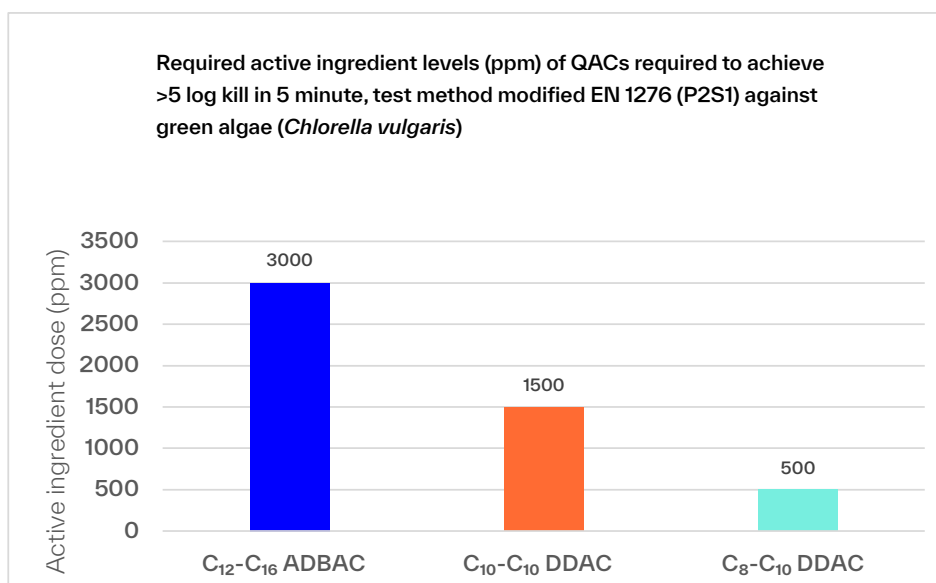


Efficacy against algae: DDAC outperforms ADBAC at 2 to 6 times lower concentration

DDAC is found to be effective against green algae at much lower doses than ADBAC. Recent data from an accredited lab suggested that against *Chlorella vulgaris* (a green unicellular algae), DDAC outperformed C₁₂-C₁₆ ADBAC when tested as per modified EN 1276 test standard. To achieve >5 log reduction, C₈-C₁₀ DDAC was required at only 500 ppm level, C₁₀-C₁₀ DDAC was required at 1500 ppm level whereas C₁₂-C₁₆ ADBAC was able to generate >5 log reduction at 3000 ppm in 5 minutes under dirty

conditions (refer to fig 3). Against other algae species known as *Raphidocelis subcapitata* which is more abundant at high salt concentrations than *Chlorella vulgaris*, C₈-C₁₀ DDAC and C₁₀-C₁₀ DDAC achieved >3 log reduction at 3000 ppm and 2000 ppm respectively whereas C₁₂-C₁₆ ADBAC could not achieve any log reduction even at 3000 ppm level (data not shown). This data indicates that in practical use conditions where elevated level of hardness and organic load may be encountered, DDAC being more tolerant to hardness and organic load will perform much better as it is discussed in the above sections.

Fig 3. concentration requirement of QACs for >5 log reduction under dirty conditions against algae





Other advantages in practical use conditions

pH: DDAC maintains its efficacy across a wide pH range at lower concentration Vs ADBAC.

QACs were deemed to be stable across a broad pH range. When tested as per EN 1276 in clean conditions at a 5 minutes contact time, C₁₀-C₁₀ DDAC retained its efficacy at lower doses compared to C₁₂-C₁₆ ADBAC across the range of pH conditions tested (highly acidic to highly alkaline) (refer to table 3).

Table 3. Stability and efficacy of QACs at different pH condition

Product	Pass concentration (ppm A.I.) [<i>P. aeruginosa</i> , EN 1276, 5 minutes, clean conditions]		
	pH 3	pH 7	pH 11
Barquat® MB-50 (C ₁₂ -C ₁₆ ADBAC)	1750	1750	1750
Bardac® 2280 (C ₁₀ -C ₁₀ DDAC)	500	500	500

Water hardness: DDAC are better tolerant (2.5 to 8 times) than ADBAC.

Water hardness affects the efficacy of QACs. The effectiveness of QACs as biocides or green removers can be reduced in hard water due to the presence of metal ions in the dilution water. These metal ions can react with the QACs forming complexes that decrease the active concentration of the disinfectant. The positive metal ions imparting hardness to water may compete with quat for the interaction sites on bacterial cell membranes. These reactions can prevent the QACs from achieving the desired biocidal effect. Additionally, hard water can also interfere with the surface activity of QACs. As described above, efficacy of quat against microorganisms is a function of interaction of positive charged polar head with negative moieties on bacterial cell membrane. Since QACs are cationic surfactants, they can bind with anions present in hard water, which may lead to a reduction in their efficacy as a green remover and a biocide. Data indicates that both C₈-C₁₀ DDAC and C₁₀-C₁₀ DDAC have a better tolerance to high levels of water hardness (>200 ppm CaCO₃) compared to C₁₂-C₁₆ ADBAC. Thus, DDAC is more suited for application as a dilutable biocide or green remover where tap water or natural source of water is used for dilution of concentrates to make ready to use biocidal products (refer



to fig 4). Tolerance to CaCO₃ Hardness of ADBAC and DDAC QACs were also evaluated as per AOAC “Germicidal & Detergent Sanitizer Method” where 200 ppm active QACs solutions evaluated against *Escherichia coli*. It was

observed that compared to C₁₂-C₁₆ ADBAC, C₁₀-C₁₀ DDAC and C₈-C₁₀ DDAC are 1.5 to 3 X more tolerant to CaCO₃ hardness (refer to fig 5, which was adapted from Ditoro, 1980).

Fig 4. Tolerance of tested QACs to different level of water hardness

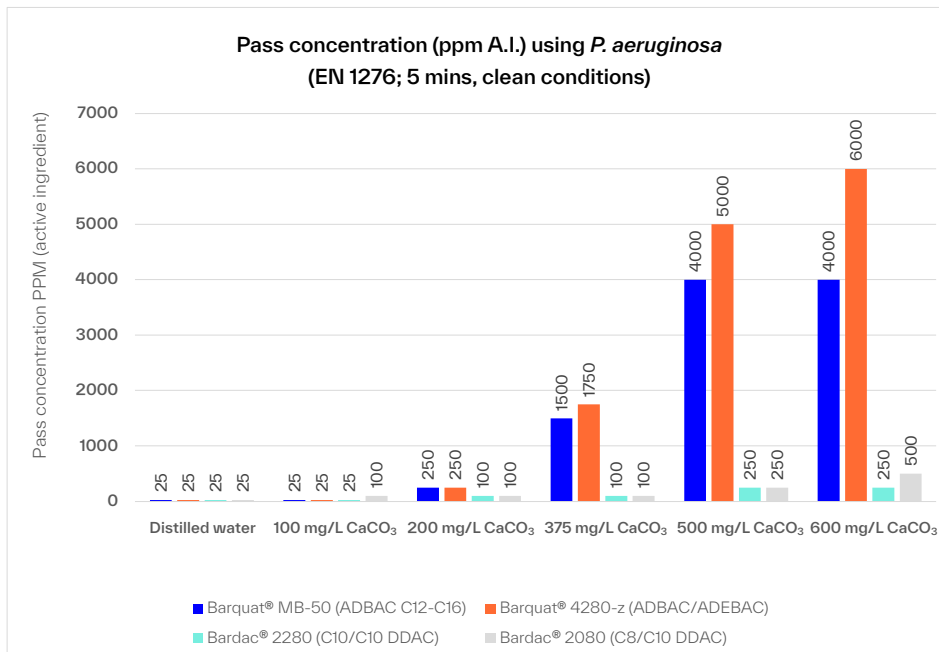
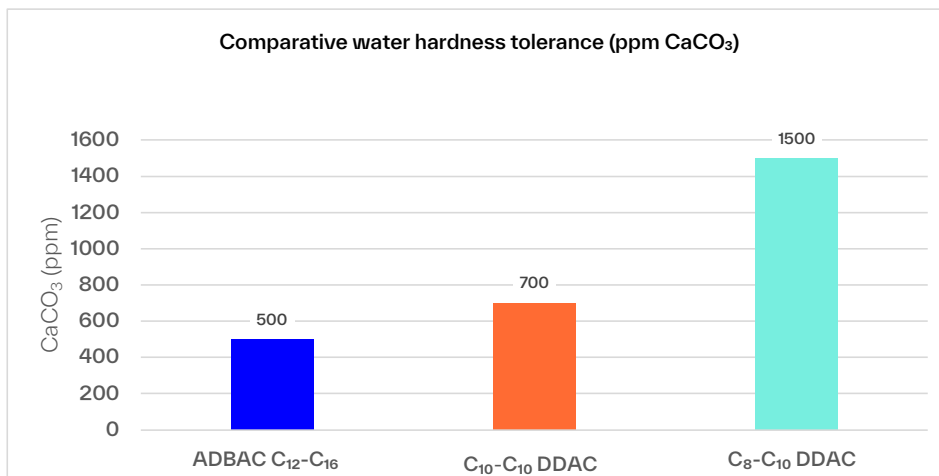
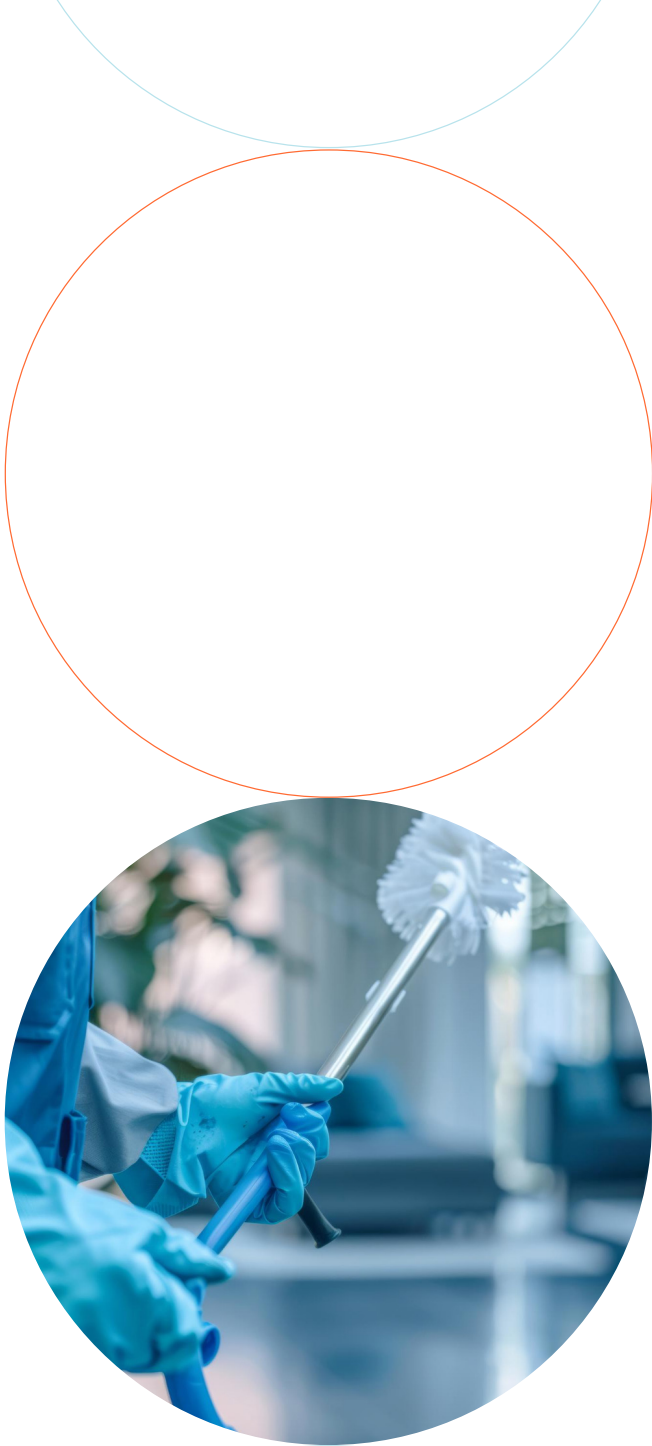


Fig 5. Water hardness tolerance of QACs at 200 ppm active ingredient level to achieve same level of efficacy (>5 log) against *Escherichia coli*





Surface tension: DDAC water solution exhibits better surfactant/wetting properties than ADBAC.

The surface tension of BARDAC® 2280 (80% C₁₀-C₁₀ DDAC) at 20 °C is concentration dependent and is 12.5% to 22% lower compared to BARQUAT® MB 80 (80% C₁₂-C₁₆ ADBAC) at a similar concentration and conditions (refer to table 4). This surface tension data indicates that in use concentrations DDAC has improved surfactant/wetting properties compared to ADBAC. Surface tension data also indicates that DDAC has a better ability to solubilize fats and thus help with cleaning compared to ADBAC.

Table 4. Wetting properties of QACs at different concentrations

Product	Surface tension (Dynes/cm at 20°C)			
	Surfactant concentration %w			
	1%	0.1%	0.01%	0.001%
Barquat MB-80 (C ₁₂ -C ₁₆ ADBAC)	33.3	33.4	50.1	63.1
Bardac 2280 (C ₁₀ -C ₁₀ DDAC)	25.9	28.1	43.0	55.2

Hazard profile: DDAC has a preferable hazard profile when compared with ADBAC.

It is important to know the hazard status of active ingredients used in the green remover application because of potential exposure possibilities for consumers and professionals. In the publicly available reports both ADBAC and DDAC are considered as non-sensitising chemistries. Sensitisation to ADBAC, although rare, does occur (Dao H Jr, et al. 2012). C₁₂-C₁₆ ADBAC is classified as Category 1 for its long-term (chronic) aquatic hazard whereas C₁₀-C₁₀ DDAC is classified as less hazardous and is put into Category 2.

C₁₀-C₁₀ DDAC exhibited 1.36X better profile than C₁₂-C₁₆ ADBAC for its long-term systemic effects by inhalation route in professional use category (refer to table 5).

Table 5. Long-term systemic effects of C10-C10 DDAC and C12-C16 ADABC

Active ingredient	End Use	Potential health effect	Route	Value
C ₁₂ -C ₁₆ ADABC	Professional	long-term systemic effects	Inhalation	3.96 mg/m ³
C ₁₀ -C ₁₀ DDAC	Professional	long-term systemic effects	Inhalation	5.39 mg/m ³

QACs concerns

The global production of QACs reached 1104.6 million US dollars, in 2022 (Sousa et al., 2023) corresponding to approximately 1 MMT of QACs worldwide. QACs are ubiquitous chemicals extensively used in medical settings, restaurants, and food production facilities (Holah, Taylor,

Dawson, & Hall, 2002). They are also used in the home as common cleaners and disinfectants. QACs have been used for around over 50 years and are considered relatively safe, but there are few concerns.

It was estimated two decades ago around 75% of QACs consumed each year are discharged into the sewage treatment system, with the rest being directly released into the environment (Patrauchan & Oriol, 2003). QACs are extensively found in industrial wastewater, domestic sewage, agricultural wastewater, surface water, and water sediment, thereby threatening the aquatic ecosystems (Tezel, 2009). The majority of QAC based green remover products in the market are formulated with C₁₂-C₁₆ ADBAC which is used extensively on external surfaces like patios, pavements, decks, roof masonry and cladding to maintain the aesthetic values of these surfaces. Theoretically, C₁₂-C₁₆ ADBAC used in this application would be washed down the drain after being used as biocides at household and hospital levels, released during product manufacturing, or run off into stormwater systems after outdoor application (Martinson et al., 2022). The toxicity of QACs, especially C₁₂-C₁₆ ADBAC, has received significant attention, because in addition to microbes, they are also harmful to the aquatic organisms, soil organisms, animals, as well as humans (Zhang et al., 2015).

Based on their better efficacy profile and other characteristics, the use of QACs can be minimised significantly by opting for DDAC over ADBAC, which can limit the overall discharge of QAC to the environment.

QACs as green remover

Algae is a slimy, green to brown-black film that grows on surfaces which are damp to wet and areas which are devoid of direct sunlight. Algal growth occurs throughout the year on many surfaces (wooden, marble, stone, gravel) including pavement, patios, masonry, decks, roof tops, floors, gravel, tarp, or bound to cooling and water systems. These algal mats not only compromise the aesthetic look of the surfaces, but they also create slippery and hazardous conditions for the users (Mergel & Dickey, 2007). Walking on algae-infested surfaces can pose a potential danger of slipping and falling because of the moist and mucous-like conditions (Berthold et al. 2021). To reduce these risks, there is a need for improved management strategies to reduce unwanted algae growth.

Algae on the surfaces can be removed by physical treatment such as pressure washing with a water jet or chemical treatment that is sprayed on the surfaces or a combination of both. Different chemicals may act by different modes of action to detach, eliminate, and destroy algae on the surfaces.

Products for the removal of algae include commercially available oxidizing agents, inorganic acids, and quaternary ammonia products (Chase & Osborn, 1984), QAC (especially C₁₂-C₁₆ ADBAC) normally used for routine cleaning of noncritical surfaces. A few products also contain C₁₀-C₁₀ DDAC.

Using an algae-removal product based on C₁₀-C₁₀ DDAC was trialled under field conditions a field trial was conducted externally on green algae (*Chlorophyta spp.*) which naturally populated the chosen substrates (wooden fencing, concrete paving & wooden decking) at the test sites. The algae removal product was applied on a concrete surface (patio slabs) by a low pressure spray (with & without brushing).

Treatment with C₁₀-C₁₀ DDAC in the field trial at 1.0% and 0.50% resulted in good levels of algal control (>80% in 14 days) on both wooden and concrete surfaces. Adding a brushing condition immediately following treatment application did not appear to have any significant impact on any of the product's efficacy scores. There was no significant algal regrowth on most of the plots even after 91/168 days post-treatment. There was a marked effect of performance against green algae with increasing levels of DDAC. No changes in color/stains to the test surface were observed following application.

Fig 6. Result of field trial with DDAC based algae removal product was applied on concrete surface (patio slabs) by low pressure spray

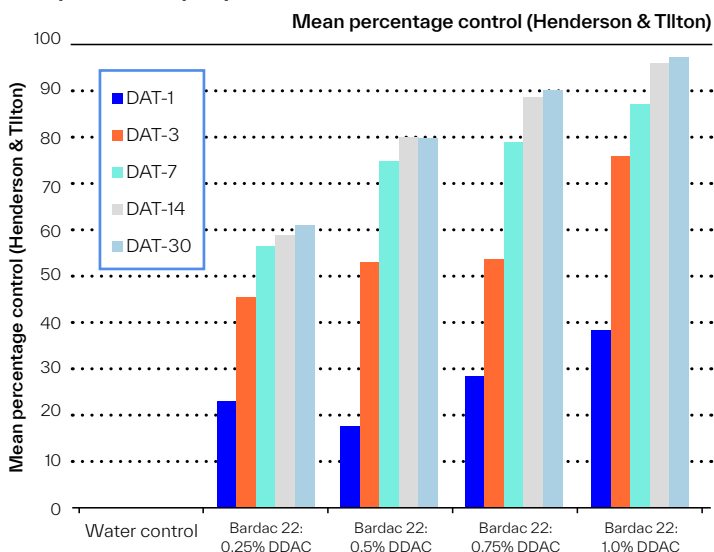
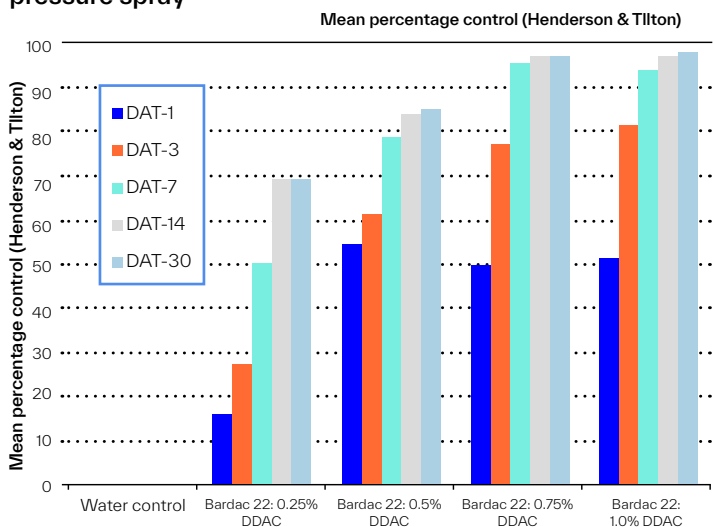


Fig 7. Result of field trial with DDAC based algae removal product was applied on wooden surface (fence) by low pressure spray





Conclusion

Using DDAC is more beneficial in all types of applications (disinfectant, algae remover) than using ADBAC. This is due to the conditions encountered in practical use (like tap water hardness and presence of organic soiling, etc.) for which C₁₂-C₁₆ ADBAC is very sensitive, meaning higher levels of ADBAC are required in much higher concentrations to achieve expected efficacy levels. Whereas C₁₀-C₁₀ DDAC or C₈-C₁₀ DDAC is more tolerant to these conditions and will achieve the necessary efficacy at up to 6-7 times lower use rates. The improved efficacy profile of DDAC is caused by its structure (2 aliphatic chains instead of an aromatic ring) which allows for better cell penetration and disruption of cell metabolism and causes higher cell membrane permeability. In comparison to ADBAC, DDAC can achieve the same or better efficacy at much lower concentrations and/or shorter contact time. This makes DDAC attractive not only from a cost-effect standpoint but also from an environmental safety perspective since less of the material will be released into the environment.

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