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Biocides for Textiles against SARS-CoV 2

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Abstract

The novel coronavirus pandemic has created an aerration of massive proportions worldwide. One of the major issues faced by most countries affected by this pandemic is the sudden quantitative inadequacy of personal protective equipment (PPE), gloves and masks, as the production rates cannot compare with the sheer expansion rate of the infection. Although the fatality rate is lower than SARS or MERS, the transmission rate is very high, which clearly indicates that protective textiles play a major role in controlling the spread. Because of the sudden spike in necessity of protective textiles, alternatives like cloth masks are being used as well, which do not have the efficiency as compared to surgical masks in terms of particle filtration, this paper will explain how antiviral biocides in different mediums play a role in reducing the burden caused by the insufficient mask production. In this paper, the properties of biocides as well as the kinds of biocides which can be utilised will be described, and products in this field which could aid in fighting coronavirus pandemic will be delineated as well.

Keywords: Novel coronavirus • Personal protective equipment • Masks • Transmission • Particle filtration • Biocides • Properties • Products

Abbreviations: SARS CoV-2: Severe Acute Respiratory Syndrome Coronavirus 2 • COVID-19: Coronavirus Disease of 2019 • QAC: Quaternary Ammonium Compounds • CS: Chitosan • FFP3: Filtering Face Pieces

Introduction

The cause of COVID-19 is SARS CoV-2 and it was initially identified in Wuhan, China, towards the end of 2019 [1]. The division of masks can be made into the following two: surgical or medical masks and N95 masks, which was designed especially for pandemics such as this but mainly for healthcare workers. Due to the pandemic, there is a worldwide struggle in mass manufacture of masks as well as personal protective equipment kits [2]. As a result, to combat this, the market of cloth masks grew but from various researches, suffice it to say that the efficiency of cloth masks is clearly lesser than that of surgical masks [3]. Another issue arises in terms of mask usage, and that is the reuse of masks. Research by Osterholm et al. suggested that masks may have higher moisture retention during its reuse, and this would compromise the physical features of the mask, which would likely increase the risk of infection [4]. As of July 26 2020, more than 1.6 million people worldwide have been affected by this coronavirus pandemic, but there is sufficient evidence to show that wearing face masks does reduce the transmission rate between individuals.

Biocides are normally defined as a chemical product that has an antiseptic and disinfectant property, so its utilization is normally not correlated with viricidalbehaviour. It is generally accepted that biocides play a role in most microorganisms like bacteria, fungi etc., as well as a virus whose structure possesses a lipid envelope [5]. SARS CoV-2 is a virus that possesses a lipid envelope [6], so the virucidalbehaviour of biocides can be utilized to improve the efficiency of reusable masks. Biocides can be used to increase the efficiency of protective gear like masks, by creating a layer over it that is virucidal in nature, thus effectively preventing the virus from crossing the barriers created by the mask [7].

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SARS CoV-2 is a positive stranded RNA virus which is coated with an envelope containing spikes of glycoproteins. The aim of most antiviral biocides is to inactivate this envelope [8]. There are several biocidal coatings available as well as in research, to help in combating the rather radical transmission propagated by SARS CoV-2 which will be discussed in the subsequent sections.

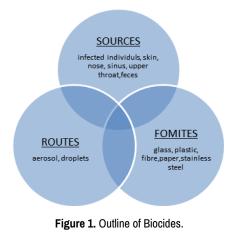
Biocides

The highly infectious SARS-CoV-2 has resulted in pandemic posing multifarious challenges caused by rapid person to person transmission. There is a deficit of PPE kits, rubbing alcohol and sanitizers due to the current COVID-19 pandemic. An alternate way of decreasing the coronaviruses from fomites and other sources is using biocides which are quite effective. The transmission of the virus needs to be controlled not only by washing hands or using an alcohol based sanitizer but also requires interventions that prevent droplet based and aerosol transmissions (Figure 1).

The virus was prevalent on surgical masks even after 7 days, it was recovered after two days from wood and fabric. Viral load and the amount of humidity are a few factors that affect the survival of coronaviruses.

A few antimicrobial agents are mentioned below that can be effectively used to provide effective hurdles to the spread of the SARS-CoV-2.

- 1. Povidone Iodine and Povidone Iodine Based Product
- 2. Hydrogen Peroxide
- 3. Sodium Hypochlorite



- 4. Peroxyacetic Acid and Acetic Acid
- 5. Chlorine Dioxide
- 6. Ozone
- 7. Ultraviolet Light
- 8. Metals

Biocides effective against SARS-CoV-2 on moist/soiled surfaces, air and skin is a requirement of high priority for transmission control. Iota carrageenan derived from red seaweed (Rhodophyceae) has shown inhibitory effects against coronaviruses and other respiratory viruses. It can avert the attachment of virus to cells and reduce viral loads in the epithelium of the nasal cavity. Povidone iodine is used in nasal sprays and might be effective as an extra measure to control the transmission of SARS-CoV-2. Different coatings could be made with the chemicals mentioned above to prevent the transmission of the virus [9].

Cross Linking

There is loss of structure and function of macromolecules when the biocides interact between various macromolecules, glutaraldehyde is the most widely used and most potent cross-linking agents. Formaldehyde is a surface-active biocide but is less effective in cross linking due to its inflexible structure. Overall, the different groups such as alcohols, phenols, and certain amino acids as well the effect of precipitation causes a loss of molecular function and structure, loss of viability, membrane damage and leakage of cytoplasmic contents [10].

Nanotechnology

In the recent decade, there has been an increase in threat for an outbreak of a global pandemic. This has led to an increase in effort to contain or reduce the effects of such a pandemic. Microbes, such as viruses are highly communicable. It is quite difficult to contain the transfer of viruses, as they are small in size and can survive under harsh circumstances. The spread of infections caused by viruses, could be the consequence of viral particles which are present in the air, entering the body along the respiratory tract. In order to safeguard the respiratory tract, protective gear, like face masks and clothing, which are made of materials that have virucidal and anti-viral characteristics can be used. The recent pandemic, 'COVID-19', is found to be in its infectious state, on copper for about 4 hours and on cardboard for about 24 hours. On stainless surfaces and plastic surfaces, the virus is seen to be active for about 2-3 days, under experimental set up. In order to stop the virus from transmitting, commonly touched surfaces or those that might come in contact with a large number of the population, must be treated with a layer or coating of antimicrobial compounds. Devices that filter particles such as the virus are also being used as an effective preventive measure. Personal protective gears like face masks, hazmat suits are also used. Since a virus particle is microscopic (20-250nm), the face masks that are used must have a filter of high filtration ability. Such type of particulate filter masks arecategorised, as 'European Standard EN 149 class FFP3'. FFP3 stands for filtering face pieces and this class of filter mediums is mostly composed of materials that are able to filter at least 99% of the harmful particles that are present in the air. This means that they have an efficiency of 99% for filtration of particles at 0.3 microns. In order to meet the benchmark of efficiency, the products need a filtering material which is composed of 2-layers [11].

Copper based Nano Biocides

Owing to the growing need for protective measures against microbes, there has been an increased requirement for advanced textiles materials. The textile material must be able to detain and decimate the viruses, in order to prevent its spread. This has given raise to the antiviral textiles which are breathable and are light fabrics, which are often used in devices that aid in respiration. The fabric must also be of good quality and shouldn't degrade

in the long run.

Generally, masks and other protective gears at present are made of antiviral materials that are metal-embedded with activated carbon components.In addition, a membranous layer can be present between the outer layers and the part that has the activated carbon embedded in it. Impressively, new studies show that the metal-embedded activated carbon material (which includes antimicrobial metal, like copper or silver), shows virucidal and antiviral characteristics as well. The mechanism of the filter works in such a way that the viruses are captured and destroyed within the structure of the cloth itself [11].

A large number of antimicrobial solutions and textile products that are used for medical, biomedical, processing of food, packaging and for the process of purification, utilise nanoparticles that are made of copper. Since, silver is relatively expensive when compared to copper, using copper as the nano biocide, helps cut down on costs for its synthesis. Another advantageous characteristic of copper nanoparticles is that, on undergoing oxidation, they form nanoparticles of copper oxide. These copper oxide nanoparticles readily mix with macromolecules or polymers to form compounds that are both physically and chemically stable, comparatively [12].

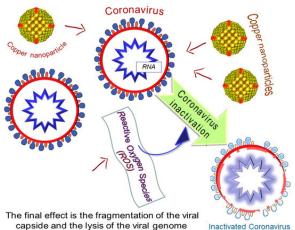
Copper oxide embedded in face masks, gives them biocidal characteristics without tampering the mask's characteristic of being a physical blockade. The enhanced ability of cupric ions to disable most forms of DNA and RNA viruses is due to the incorporation of hydrogen peroxide to it. Hydrogen peroxide, then converts into its highly reactive hydroxyl radical, that incorporates itself into the nucleic acids, proteins and lipids of the microbe, eventually killing it [13,14] (Figure 2).

Silver based Nano Biocides

Towards the concluding stage of the manufacturing process of textile, a Swiss technology known as HeiQViroblock NPJ03 comes in handy. This intelligent technology has proven to be effective against COVID-19, 99.99% of the time. This can be used on various PPE like face masks, medical gowns, air filters and medical gloves that are especially non-woven.

HeiQViroblock uses a unique combination of silver technology and vesicle technology as a booster for antiviral and antibacterial effects. The silver technology is used to attract the oppositely charged viral particles, which then combines them indefinitely to their sulfur groups. Then the liposomes affect the viral membrane, by depleting the amount of cholesterol present in it, within minutes. This ultimately destroys the virus by the action of silver nanoparticles as shown in Tables 1 & 2.

According to the ISO 18184 and 20743, silver based Nano biocides show strong antiviral and antibacterial properties against enveloped viruses respectively. It is suitable for all types of fiber and it is completely safe and sustainable as per the cosmetic grade which is 72% bio based carbon.



capside and the lysis of the viral genome

Figure 2. Inactivation of coronavirus, by copper nanoparticles. Adapted from: [15].

SI No.				
	Technique	Outcome	Examples	
	Reducing and Oxidising Factors	Loss of function and structure, due to electrons being removed from large molecules.	Halogens: Chlorine, Iodine etc.	
	Cross Linking and Coagulation	Gives rise to cross linking and interactions amongst large molecules, which causes coagulation and clustering.	Aldehydes: formaldehyde, glutaraldehyde	
	Energy Transfer	Energy transfer to large molecular bonds, which causes the loss of function and structure.	Heat, radiation such as UV, light etc.	
	Other Structure Disrupting Agents	Disorientation of structures of particular large molecules and their eventual activity loss.	QAC's and metals such as silver, copper etc	

Table 1. Mechanism of Action of General Biocides with Suitable Examples [10].

Table 2. The promising biocidal efficacy of textiles treated with HeiQViroblockNPJ03 [16].

ID	Agent	Log reduction	% reduction
LS20-00319-6	H3N2 (Human Influenza A)	4.72	99.99%

Properties:

- 1. Resists wool up to 5 dry cleanings
- 2. Lasts at least 30 washes at 60 degree Celsius
- 3. Hypoallergenic
- 4. Provides germ resistant and self-sanitizing surface
- 5. Antiviral and antibacterial technology

Antiviral efficacy test: Disposable face masks of nonwoven material that are coated with HeiQViroblock NPJ03 have been tested according to the ISO 18184 standard and have shown excellent antiviral efficacy.

According to the Aerosol Challenge (ASTM F2101) the test was performed with modifications on the virus. The ASTM F2101 test is as follows:

1. The test mask is sealed and mounted in a test chamber.

2. The aerosol of the target virus is delivered via a nebulizer to the upstream side of the face mask.

3. Below the mask a collection dish is placed to collect the aerosol droplets that penetratethe sample mask.

4. The decrease in infectivity is calculated as an indicator of effectiveness with and without the mask. The deviation in log reduction of Δ =1 shows us 10x and Δ =2 shows us 100x

HeiQ highly recommends testing the fabric that has been treated, for mill validation and trademark licensing. An antiviral test thus can be undertaken, that is ISO 181841 with the encapsulated virus H1N1 or H3N2 or a type of Coronavirus. Ultimately, HeiQ will endorse testing laboratories, but will notperform the antiviral tests [16-18].

Quaternary Ammonium Compounds

Quaternary Ammonium Compounds (QAC) are detergents that are cationic in nature that play a biocidal role in fomites. Given the situation caused by the pandemic, almost every inanimate object has become a potential fomite [19]. QAC's aim to form micelles through the reduction in surface tension.

Structure of QAC

The simplest representation of the structural composition of a QAC is as a cation and an anion as shown in Figures 3-8. Four groups surround centralised nitrogen, and this can exist in a diverse range of structures [20]. This comprises the cationic region of the QAC. The anion most commonly comprises bromine or chlorine, which forms a bond with the cationic portion of the QAC to form a salt.

The biocidal activity of QAC's varies on the basis of variations created because of the nature of the QAC. The nature of QAC's distinctions is due

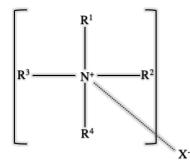
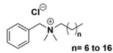
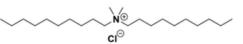


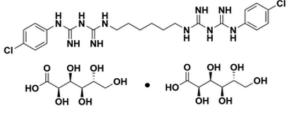
Figure 3. General Structure of Quaternary Ammonium Compounds [20].



Benzalkonium Chloride (BAC)



Didecyldimethylammonium Chloride (DDAC)



ChlorhexidineGluconate (CG)

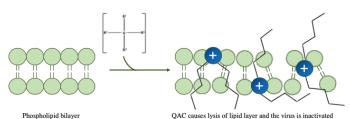
Figure 4. Some Examples of Virucidal QAC [22].

to the R group's nature, aromatic group presence, C chain branching as well as the quantity of N atoms [21] (EDIT diagram of structures here)

There also exists antimicrobial products with an amalgamation of QAC's for the sole aim of increasing its efficiency towards a certain sect of microorganisms [22,23].

Mechanism of Action

QAC's are known for their hydrophobic activity towards viruses that are enveloped with lipids. McDonnell offered the following steps to describe the mechanism of action followed by QAC's:



QAC causes lysis of lipid layer and the virus is

Figure 5. Mechanism of Action of QAC [25].

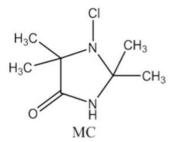


Figure 6. Structure of MC, Synthesized N-halamine compound [33].

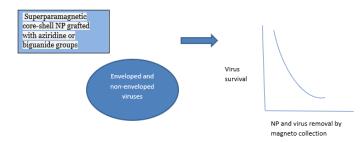


Figure 7. Superparamagnetic core shell NP grafted with aziridine and effect on virus.

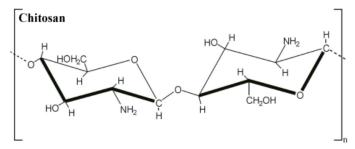


Figure 8. Structure of Chitosan.

1. QAC would first adsorb to the cell wall and subsequently penetrate the cell wall [20]

2. It would then interact with the lipid membrane of the virus, effectively degrading it

3. This degradation then results in an inactivation of the virus, as it can no longer bind to host cells because SARS CoV-2 relies on the ACE2 receptors to bind to the host cell, which is present on the lipid envelope of the virus [24].

Current Application in COVID-19 Pandemic

Currently, QAC's are available in the form of disinfectants, sanitizers and sprays for the surface and environments. Ways to incorporate it on textiles are currently being researched. A couple of researchers at the National Centre of Biological Sciences (NCBS), Bangalore, have created a textile coating, composed of QAC's, and seems to be showing good lab results till now. According to the lead researcher, Dr. Praveen Kumar Vemula, there are two methods for the utilization of the coating:

1. Application of the solution on the cloth, like the mask or PPE kit, and then perform heat fixing to help with the attachment of molecules on the surface of the textile

2. Textiles with the compound priorly fixed to it can be sent for manufacture into gloves, masks, PPE kits etc.

As of now, they are clear that it cannot be applied in the form of an ointment, and it may have unknown dire consequences to the skin because there has been no testing done yet to see its capability on skin. Their study has shown that the solution retains its biocidal property efficiently even after 25 washing cycles. While the mask acts as a physical barrier, this will inactivate the virus post contact [26].

6. N- Halamines

The compound N-halamine is the one that has one or more covalent bonds between nitrogen and halogen(Cl,Br or I). Thebond between them is formed by halogenation of amide, amine or imide groups [27]. It has biocidal property due to the oxidative state of halogen. Also these biocidal properties can be regenerated even after long-term use and washing [28]. The compound N-halamines is usually obtained from hydantoins, this represents a group of compounds that is characterised by different biological activities including antiviral, antibacterial, fungicidal and many more. The N-halamine polymers show their biocidal properties based on the chemical structure of hydantoin[29]. N-halamines that are reactive in nature, contains reactive agents that can attach onto the fibres by a covalent bond. Now this makes the textiles durable and antimicrobial in nature [27]. The N-halamines are attached onto the textiles through cross linking. The agents used for cross linking are 1,3-dimethylol-5,5-dimethyl- hydantoin (DMDMH) and certain polycarboxylic acids. A group of N-halamine copolymers added with epoxide, hydroxyl groups and silane were synthesized and coated onto the cotton fabric due to the formation of chemical bonds.

N-halamines with one or more N—Cl bonds have been integrated onto the fibres [27]. It was also found that MC (1-chloro-2,2,5,5-tetramethyl-4imidazolidinone), a type of N-halamine, was coated on non-woven fabrics that gave it antimicrobial property to act against the bird flu also known as avian virus. Also the chlorine bonded to N-halamines provides antimicrobial property. This is used in mask making. Currently many masks are coated with MC due to their antiviral activity.MC usually shows the same ability to inactivate the virus and to disintegrate the viral RNA since it has active chlorine as their antimicrobial element. Usually these non-woven fabrics are coated by pad dry technique [30,31]. Also N-halamine compounds that are based on antimicrobial agents are used as add on for polymers to provide antimicrobial functions. Example: 1-chloro-3-alkyl-5,5-dimethylhydantoin (CADMH) added into polystyrene as antimicrobial additives. These provide the polymeric material with potent and durable antimicrobial properties that are basically used for gloves [32].

Poly Biguanides

Biguanides are popularly used as drugs for oral anti-diabetics and have shown a huge promise in oncology [33,34]. Poly biguanides gained importance when they were studied for their antimalarial properties. N¹·N⁵ substituted biguanides have been found to have germicidal, antimalarial and antiviral properties.

The mammalian target of rapamycin (mTOR) signallingresponds to nutrition, amount of energy available, hormones and modulation of protein synthesis using mitogens. The PI3K (or) AKT (or) mTORsignalling responses can represent a novel drug target for strategies of therapeutic intervention. Buformin which belongs to a class of biguanides may be used as an effective treatment for coronaviruses.

Biguanides and its derivatives were tested for in vitro antiviral activity against polio, vaccinia and influenza A viruses. It was found that alkyl derivatives were more effective against polio and influenza.

The Polycationicsuperparamagnetic nanoparticles core-shell particles with

functional biguanides or moieties of aziridine bind to bacteriophage MS2, enveloped viral haemorrhagicsepticaemia virus (VHSV), nonenveloped infectious pancreatic necrosis virus (IPNV), and herpes simplex virus HSV-1 and inactivate them. Then magneto collection can be used to remove the virus-particle complexes from the aqueous milieu

Chitosan

Structure

Chitosan (CS) is a polysaccharide which is a deacetylate derivative of chitin. The D-glucosamine residues in this linear polymer are liked through β 1,4 linkages. The size of the molecule usually varies according to the mean degree of polymerization or mean molecular weight.

Properties

CS is naturally known to be non-toxic, biocompatible and biodegradable. CS and its derivatives have been distinguished to have various biological properties such as anti-cholesterol, antiviral, antibacterial and antitumor. These properties are being investigated in numerous medical and pharmaceutical applications such as drug delivery, tissue engineering, wound dressings and cell encapsulation.

CS has the ability to resist viral infection in plant and animal cells, and prevents phage infection from further developing in microbial cultures. This immune fighting response by CS to protect organisms from and kind of stress or disease has brought considerable interest to the textile industry. It has been proven that the polysaccharide with high degree of polymerization has better antiviral activity such as suppressing local necrosis of tobacco leaves by tobacco mosaic virus in plants.

CS was first proven to express defense responses against abiotic and biotic stresses in Pisumsativum L. and Solanumlycopersicum L. This led to the development of nanoparticles based CS to deliver nutrients and chemicals to plants efficiently.

In advent of the current pandemic, many studies have been undertaken with modified versions of chitosan such as N-(2- hydroxy-propyl)-3-trimethylammonium chitosan chloride known asHTCC, cationic modified CS and its hydrophobically modified derivative known as HM-HTCC.

It has been found that HTCC hinders the virus by blocking the interaction of the virus with the receptor and thus blocking the entry.

Current application

CS based coatings have already been well established for its antibacterial property in the textile industry. But it has never been used as an antiviral coating to prevent the entry of viruses. This coating can be applied onto various PPE like masks and gloves. Especially, during this pandemic this CS coating could be a potential advantage for the front line workers.

However, this method has not been exploited much for its antiviral property. But CS has proven to provide sterile conditions and is compatible when combined with any textile fabric. This coating could be applied through various treatment methods like:

- 1. Spraying onto the fabric
- 2. Screen printing the coating into the fabric with appropriate binder
- 3. Bath exhaustion process
- 4. Padding process

Thus, CS based textile could lead to a new generation of smart and innovative PPE that delivers properties that are beneficial to the user.

Conclusion and Future Prospects

Individuals worldwide seem to be conflicted about the usage of various

protective textiles to curb the rampant transmission of this virus. The WHO initially tried to control usage of masks because of the sudden lack that was being faced by frontline healthcare workers. Now, more research has taught us that wearing a mask is imperative not just for one's protection, but more to prevent a spread on the off chance that an individual might be asymptomatic without their knowledge. The WHO further changed their stance on mask usage, and now suggests that in situations where social distancing cannot be practised, a mask should be worn.

The rapid transmission rate of SARS CoV-2 has shaken healthcare industries worldwide, and it has reached the stage where health care workers are reusing their protective equipment, which is quite dangerous when dealing with a virus with such high efficiency of transmission. Biocides will play a significant role in easing the load that has been unceremoniously placed on them. Various protocols are being utilised to reduce or control the virus transmission, like social distancing, usage of protective textiles as well as using agents for disinfection or sanitization.

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