
Nanofibers functionalized with surfactants to Eliminate SARS-CoV-2 and other airborne pathogens

Nanofibras funcionalizadas com surfactantes para eliminar SARS-COV-2 e outros patógenos presentes no ar

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ABSTRACT

The recent SARS-CoV-2 pandemic brought to light the difficulty in controlling the pathogenic bioaerosols present in the air. So, several studies have sought efficient and mainly sustainable technologies to develop new filtering media and new biocidal and virucidal agents. Filter media composed of nanofibers stand out for having high collection efficiencies and high permeability. For this reason, they have been widely used in filters for indoor environments and in face masks. Combined with nanofibers or conventional filtering media, the addition of quaternary ammonium surfactants to provide biocidal action proves to be an ecologically sustainable alternative. Thus, the present work reviews these filtering mechanisms, their applications, and perspectives for novel uses of these technologies in engineering and materials science.

Keywords: SARS-CoV-2; Air filters; Electrospinning; Bioaerosols; Biocide;

RESUMO

A recente pandemia de SARS-CoV-2 trouxe à luz a dificuldade no controle de aerossóis patogênicos presentes no ar. Portanto, vários estudos têm procurado tecnologias eficientes e principalmente sustentáveis no desenvolvimento de novos meios filtrantes e novos agentes virucidas e biocidas. Meios filtrantes compostos por nanofibras se destacam por ter alta eficiência de coleta e alta permeabilidade. Por este motivo eles tem sido aplicados em filtros para ambientes internos e mascaras. Combinados com nanofibras ou meios filtrantes tradicionais, a adição de surfactantes quaternários de amônia para prover ação biocida tem se provado uma alternativa sustentável. Portanto, este trabalho revisa os mecanismos de filtragem, suas aplicações e perspectivas para o uso dessas tecnologias em engenharia e na ciência de materiais.

Keywords: SARS-CoV-2; Filtros de ar; Eletrofição; Bioaerossóis; Biocida;

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INTRODUCTION

Today, people spend around 90% of their time indoors, turning themselves into an "indoor generation" (EU, 2003). In this context, airborne diseases become an important issue, especially for crowded places like hospitals, universities, or public transport (BALAGNA *et al.*, 2020). Even in outdoor areas, the possibility of virus spread remains. One evidence is the event on 26 of September at the Rose Garden of the White House. At least eleven people were infected with the new coronavirus, including the President of the United States (MANDAVILLI; TULLY, 2020). So, protection against air contamination is crucial, improving the indoor infrastructure of buildings to preserve patients, health workers, caregivers, and people in general.

In the SARS pandemic of 2003, two of the Metropole Hotel guests in Kowloon, Hong Kong, spread the SARS-CoV-1 virus to 23 other people, from the 9th floor to the 7th floor of the building. Those people recently infected traveled to other countries spreading the virus worldwide (HANAGE, 2017). At the start of the SARS-CoV-2 pandemic, various cruise ships with thousands of people on board imposed the passengers' isolation in their cabins, like the Diamond Princess cruise ship in Yokohama (ZHANG, S. *et al.*, 2020). Their objective was to limit the contact and proceed with adequate hygiene methods. But, even with the isolation, many were still being infected with the new coronavirus. Morawaska & Cao (2020) suggested that the ventilation system was responsible for the virus' continuous spread between the cabins (MORAWSKA; CAO, 2020).

The evidence of airborne transmission of diseases, proposed since the SARS pandemic in 2003 (YU *et al.*, 2004), has become more robust in the recent pandemic (GREENHALGH *et al.*, 2021). Studies show that SARS-CoV-2 can remain in aerosol particles for longer than 3 hours (VAN DOREMALEN *et al.*, 2020). It was also detected in the air and ventilation systems of houses (SHANKAR *et al.*, 2022), hospitals, nursing homes, and exhaustion of ferryboats (MOUCHTOURI *et al.*, 2020).

One of the most applied methods for removing aerosols from the air is the filtration process (ALIABADI, 2017). In the cases mentioned previously, adequate air filters can minimize the disease's spread, catching and killing the virions traveling through ventilation systems. Recently, air filtration with antiviral activity has received more

attention, preventing virus spread through the air. The benefits are the rapid inactivation, minimizing the number of active virions blowing off the filter media (PYANKOV *et al.*, 2008).

New strains of SARS-CoV-2 have been surging since the beginning of the COVID-19 pandemic. Variants like the United Kingdom strain (IACOBUCCI, 2021), the South Africa strain (TEGALLY *et al.*, 2021), the Brazilian strain (FARIA *et al.*, 2021), the Indian strain (ALAI *et al.*, 2021), and the later omicron strain (XU *et al.*, 2022) has been motive of preoccupation. New strains showed stronger interactions with the binding receptors of the host cell, resulting in higher infectivity (DASH *et al.*, 2021). They spread worldwide, reinflating the pandemic by causing new infection waves (RENDANA; IDRIS, 2021). So, the necessity for materials that can eliminate such bioaerosols during the traveling process is urgent.

AIRBORNE PATHOGENS SPREAD MECHANISM

The new Coronavirus (SARS-CoV-2) has 60 to 140 nm in diameter and spikes about 9 to 12 nm (ZHU, N. *et al.*, 2020). It possesses improvements on its spikes, making possible better affixation of the virions in carrier particles (LEUNG; SUN, 2020). After being expelled from an infected person, its virions can be aerosolized by droplets or attach to solid particles (LEUNG; SUN, 2020). It was expected that the particles with an attached virion are too heavy to remain in the air and then descend to the ground (STADNYTSKYI *et al.*, 2020). However, after being expelled by the body, droplets start to evaporate their liquid portion and shrink (BOUROUIBA *et al.*, 2014; HOWARD *et al.*, 2021; NICAS *et al.*, 2005). Some become smaller, being more influenced by the airflow than gravity, making the droplet travel long distances (AYDIN *et al.*, 2020; MORAWSKA *et al.*, 2009), reaching distances greater than 3 m from its source (FENG *et al.*, 2020). Some viruses can remain infective even after hours, especially in higher relative humidity (OSWIN *et al.*, 2021).

During the flight, the airborne virions can be transferred to ambient aerosols. The excellent ability to attach makes it possible for the virions to adhere to small solid particles, resulting in aerosols in the proportion of the virion size (60 to 140 nm). Minor

combined aerosols (*i.e.*, virion and particle) will reach longer distances (MORAWSKA; CAO, 2020). This phenomenon is similar to fine particulate pollution suspended in the air. As finer as the particles, they can travel more distance (LEUNG; SUN, 2020), is already detected in the air near infected people (SHANKAR *et al.*, 2022). This effect explains how the SARS-CoV-2 spread, primarily indoor (MORAWSKA *et al.*, 2020), and can remain in the air for periods longer than 60 min, as shown studies with MERS coronavirus (PYANKOV *et al.*, 2018).

Both aerosols and larger droplets can carry viruses (BOUROUIBA, 2020; GRALTON *et al.*, 2011). During talking, breathing, and coughing, infected people, can generate a significant amount of submicron particles, including many viruses (RENGASAMY *et al.*, 2010). Studies show that 87% of exhaled particles of patients infected with influenza were minor than 1000 nm in diameter (FABIAN *et al.*, 2008). The number of particles emitted is so high that another person's inhalation is unavoidable, even when wearing surgical masks (CHENG *et al.*, 2021). Particle size and concentration vary from one study to another and are summarized in table 1.

Table 1: Data from different authors of average diameter and concentration of particles expelled during coughing, talking, or breathing.

Particle average diameter (µm)	Particle concentration (particles L ⁻¹)	Reference
0.09-3.00	150-2000 ^b ; 100-350 ^c	(FAIRCHILD; STAMPFER, 1987)
0.32	14-3230 ^c	(EDWARDS <i>et al.</i> , 2004)
13.5 ^a ; 16.0 ^b	2400-5200 ^a ; 4-223 ^b	(CHAO <i>et al.</i> , 2009)
3.5-5.0 ^b	1100 ^b ; 100-1100 ^c	(MORAWSKA <i>et al.</i> , 2009)
1.6, 2.5, 145 ^b ; 1.6, 1.7, 123 ^a	1, 69, 85 ^b ; 12, 16, 87 ^a	(JOHNSON <i>et al.</i> , 2011)*
12-29 ^b ; <10 ^c	1080 ^b ; 540 ^c	(ALSVED <i>et al.</i> , 2020)

^acoughing; ^btalking; ^cbreathing; *three different methods were used in this study to avail the particles size diameter and concentration.

Observations have found that aerosol particles with less than 5 μm of diameter contain more viruses than larger droplets (FENNELLY, 2020; LEUNG *et al.*, 2020). A possible explanation is that smaller aerosols are produced in the lower respiratory tract that has a higher viral load during infections (BAKE *et al.*, 2019; JOHNSON; MORAWSKA, 2009). Unfortunately, particulate matter minor than 2.5 μm of diameter ($\text{PM}_{2.5}$) can penetrate the respiratory system, reaching the alveoli and even the cardiovascular system (CHENG *et al.*, 2021; NEUPANE *et al.*, 2019).

FACE MASKS

Face masks are an item used for personal protection, and they have been used for medical purposes since the 17th century (GOH *et al.*, 2020). In 1900 their use was diffused, aiming to reduce nasal and oral bacteria in surgical procedures (BELKIN, 1996). In the last decade, the use of masks on prevention of bioaerosol gained attention again, caused by pandemics like influenza (BOOTH *et al.*, 2013; SUESS *et al.*, 2012), Middle East Respiratory Syndrome (MERS) coronavirus (AL-TAWFIQ *et al.*, 2019), and even Ebola (OSTERHOLM *et al.*, 2015). With the recent pandemic of SARS-CoV-2, the mask usage has become essential, leading researchers to expand studies on the field (GANCZAK *et al.*, 2021; IPPOLITO *et al.*, 2020; SELVARANJAN *et al.*, 2021; TABATABAEIZADEH, 2021). The area's cutting-edge technology developed new face masks with lyophilized CRISPR sensors capable of detecting pathogens as SARS-CoV-2 *in situ* (NGUYEN *et al.*, 2021).

During a pandemic, health care workers' protection relies on personal protective equipment (LEPELLETIER *et al.*, 2020), and facemasks of high performance such as N95 and FFP2 models have already proved their efficacy against the SARS-CoV-2 and other pathogens (CHENG *et al.*, 2021; GRINSHUPUN *et al.*, 2009; LINDSLEY *et al.*, 2021). Unfortunately, this material is insufficient to attend to the high world demand and needs to be directed to health care workers (IPPOLITO *et al.*, 2020; THAPER *et al.*, 2021).

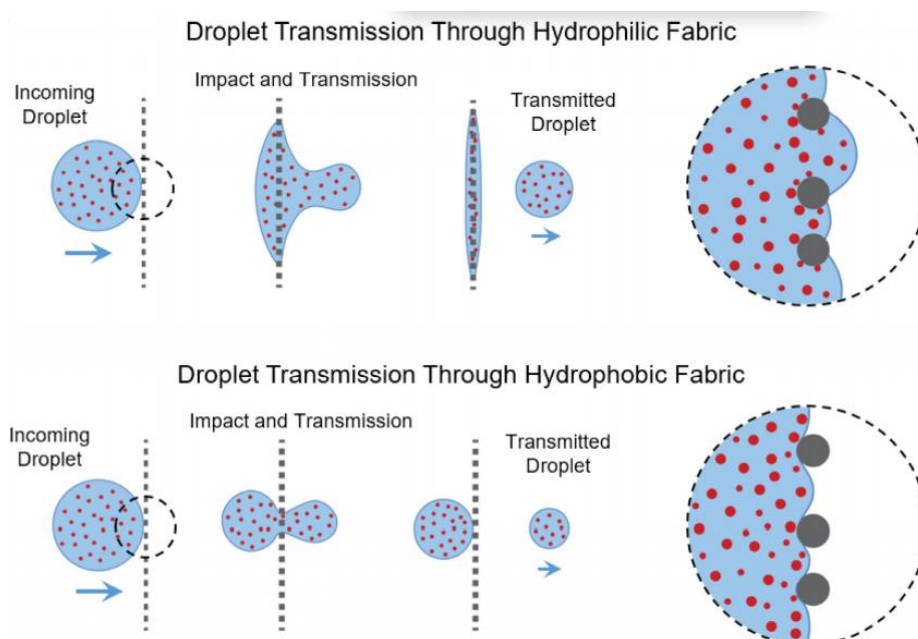
The use of masks becomes a security symbol in a pandemic (GOH *et al.*, 2020) but can be a false sense of protection. Shortages in supply force the population to use

more accessible masks, such as surgical and cloth masks. Household materials are unsuitable for retaining particles, and cloth masks were not designed for respiratory safety (RENGASAMY *et al.*, 2010). They have a wide range of filtration efficiency, varying from one material to another (MORAIS *et al.*, 2021). The utilization and moisture retention caused by the cloth materials' physical properties can be potential factors that increase infection rates (MACINTYRE *et al.*, 2015). Washing cloth masks also stretch the fabric, altering the pore size and consequently decreasing the filtering efficiency of the material (NEUPANE *et al.*, 2019). Even high-performance masks during cleaning procedures can lose their capability to retain particles, becoming unsuitable to use (OU *et al.*, 2020).

Especially in cloth masks, small aerosols can penetrate through the mat pores as projectiles or carry by the airflow, specially droplets in the range between 0.3 to 2 μm (KÄHLER; HAIN, 2020). Droplets with enough momentum can surpass the barrier of the fabric pores (as described in figure 1). Shear stress and surface tension can force the droplet to squeeze through the interfiber spaces (AYDIN *et al.*, 2020), and they may reach the respiratory tract (LÖNDAHL *et al.*, 2007). Viruses carried by the liquid particle can remain viable on the surface mask, remaining on the retentate portion of the droplet (OSTERHOLM *et al.*, 2015).

Even though the efficiency of masks has pros and cons, the general usage by the population has already proved to diminish virus transmission (BROOKS *et al.*, 2020; CHIRIZZI *et al.*, 2021; CHU *et al.*, 2020; TABATABAEIZADEH, 2021). For example, tests with cloth masks against particles emitted by diesel combustion (ranging between 30 – 500 nm) obtained efficiencies between 15 to 57 % (SHAKYA *et al.*, 2017), so still more effective than no masks at all. A possible way to improve the filtration efficiency of cloth masks is to use multilayers, imposing additional barriers to the penetration of the particles (AYDIN *et al.*, 2020; CRILLEY *et al.*, 2021; KONDA *et al.*, 2020; NICOSIA *et al.*, 2015). But cloth masks still not being suitable for respiratory protection. The goal is to functionalize cloth materials with a biocidal material that can remain on the fiber surface and eliminate the pathogen (*i.e.*, viruses, bacteria, and fungi) without being dangerous to the wearer (DE ALMEIDA *et al.*, 2021).

Figure 1: Scheme showing how the particles can squeeze through pores of cloth masks with hydrophilic and hydrophobic materials.



Adapted from Aydin *et al.* (AYDIN *et al.*, 2020).

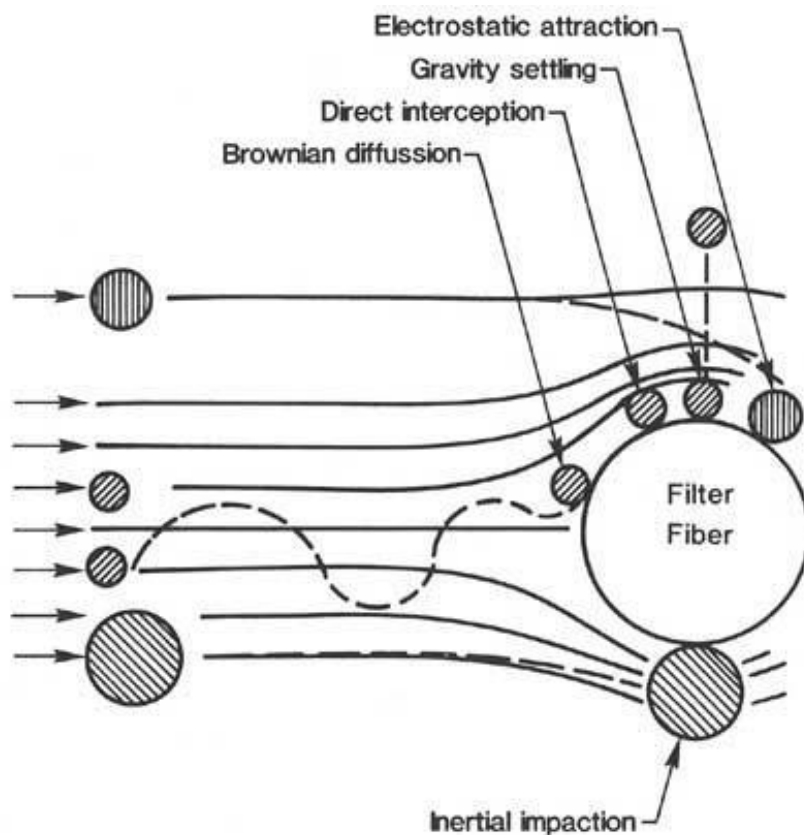
RETENTION MECHANISMS ONTO FIBER FILTER MEDIA

The principal mechanism of collecting aerosols by face masks and air filters is the retention onto micro or nanofibers. Nanofibers are a class of materials extensively used in the last decade as air filter media due to the low-pressure drops (SAMBAER *et al.*, 2012; SUNDARRAJAN *et al.*, 2014). Its channels are commonly sinuous and interconnected, granting low air resistance and high filtration efficiency, essential for air filtering (ZHANG *et al.*, 2019). Many industries employ these materials in their air filters to clean large amounts of air 78, even in medical applications (CHANG *et al.*, 2020; KRAVTSOV *et al.*, 2000). Commercial filters typically use microfibers with low air resistance and limited fine particle removal efficiency (WANG *et al.*, 2016). It can be a problem since small particles frequently carry compounds due to their large surface area (DIEME *et al.*, 2012; KENDALL *et al.*, 2004).

Particles and aerosols can be classified accordingly with the Particulate Matter (PM) diameter range, being PM 0.1 ($< 0.1 \mu\text{m}$), or ultrafine; PM 2.5 ($0.1 - 2.5 \mu\text{m}$), or

fine; and PM 10 (2.5 – 10 μm) or course (KADAM *et al.*, 2016). Since the SARS-CoV-2 has an average diameter ranging from 60 to 140 nm, it can be defined as ultrafine (PM 0.1) or fine (PM 2.5) particles. Common air filtering methods can effectively remove PM 2.5 (XIONG *et al.*, 2017). However, the typical sieving process does not collect such particles onto filters. Fibers in the nanometric scale exhibit properties that enhance filtration efficiency, such as high surface energy and enhanced surface reactivity (MATULEVICIUS *et al.*, 2014; THAKUR, 2014; XIA *et al.*, 2018). The PM's removal process by filters involves a dynamic adsorption and desorption process, and stronger interactions increase the filtering efficiency (ZHU, M. *et al.*, 2020). The particles retention occurs due to three distinct mechanisms: the flow hydrodynamics that passes through a single fiber; small particulates stochastic movement; and electrostatic mechanism caused by a charge in the particles or fibers. The retention mechanisms in the filtration (figure 2) can be classified according to as:

Figure 2: Different mechanisms of particle capture by fibers during the process of air filtration. Particles are removed from the streamline and collide onto a retention site.



Addapted from Hong & Fitch (HONG; FITCH, 1985).

Direct interception: particles that find a retention site along the fluid trajectory.

Inertial impaction: particles with mass greater than the carrier fluid have difficulties following the streamlines. Their trajectory "thrown" them away into a retention site.

Diffusion: small particles do not follow a fluid streamline but diffuse across the fiber mat. In this process, they may reach a retention site. Brownian motion is higher in smaller particles and decreases with the increment in the fluid velocity.

Gravity: at low velocities, particles with a different density than the fluid can deviate from the streamlines to a retention site. Fluids with higher viscosity and velocity reduce the gravitational effect, while heavier particles are more subjected to it.

Electrostatic Attraction: particles that possess dipoles or different charges from the filter fibers can be attracted to their surfaces.

Hydrodynamic Effects: due to the non-uniformity of the flow field, nonspherical particles tend to migrate to the outside of a fluid streamline and may enter in a retention site.

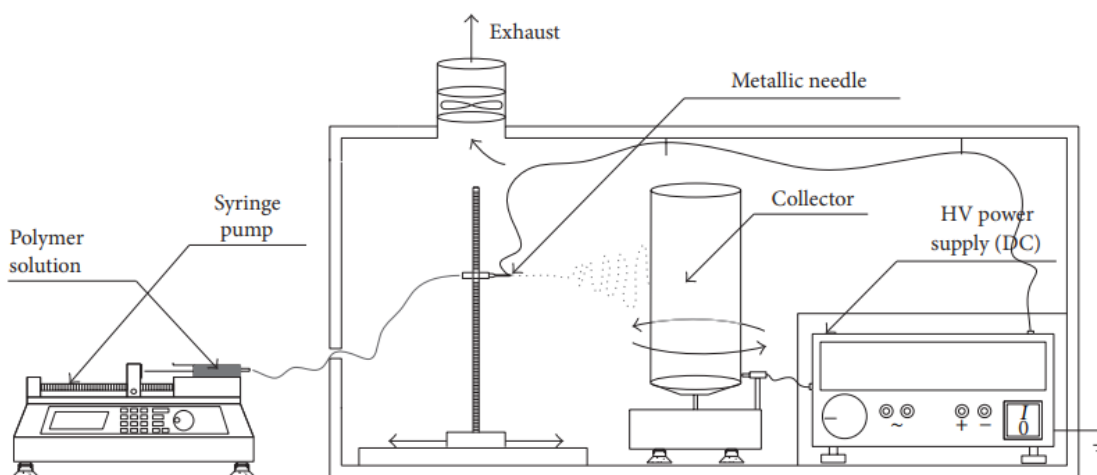
One or another mechanism can dominate over the others, depending on the particle size (KRAVTSOV *et al.*, 2000). Aerosols in the range of 1 μm to 10 μm are more influenced by hydrodynamic effect (ballistic energy) or gravity forces. In sizes from 100 nm to 1 μm , the predominant mechanism becomes diffusion caused by Brownian motion. Diffusion is the primary filtration phenomenon for the SARS family due to its tiny diameter (DAS, O. *et al.*, 2020). The mechanical capture by interception is also a relevant effect (LEUNG; SUN, 2020). Nanometer-sized particles (less than 100 nm) can easily slide through the pores on the mat, so electrostatic attraction predominates over other phenomena. Low mass particles are attracted to the fibers and then bounded by the electric field (KONDA *et al.*, 2020).

NANOFIBERS IN FILTRATION PROCESS

Nanofibers are versatile materials that can be successfully used as high-efficiency filtration membranes, capable of capturing organic and inorganic particulate materials, including viruses and microorganisms (*e.g.* fungi, bacteria).

Manufacture: There are many techniques to produce micro and nanofibers, such as melt-spinning and laser spinning (TOMISAWA *et al.*, 2017). Electrospinning stands out among those because of its versatility and the applicability of different materials, generating fibers with controllable morphology (WANG *et al.*, 2018). The process is described in figure 3.

Figure 3: Schematic design of nanofibers production by electrospinning technique.



Addapted from Matulevicius *et al.* (MATULEVICIUS *et al.*, 2014).

The basic concept is to apply a high voltage electrical field between a needle and a metal plate at a defined distance. A solution of an electrostatic and viscous polymer is then squeezed through the needle and enters the electrical field (AHN *et al.*, 2006). The first pendant droplet at the edge of the needle tends to form a cone shape called the Taylor cone (YARIN *et al.*, 2001). Electrical charges accumulate on the polymer surface, creating a repulsion force capable of overcoming the polymer surface tension. The electrostatic repulsion stretches the polymer from the needle toward the metal plate, elongating the fiber to nanoscale dimensions (MELI *et al.*, 2010). The solvent evaporates during the trajectory between the needle and the collector, allowing the polymer to solidify on the metal plate. The metal plate is covered with a collector material, commonly aluminum foil. A series of variables can be changed to improve the properties of the fibers, like solution concentration, the molecular weight of the polymer, surface tension,

conductivity, solvent, applied voltage of the electrical field, and flow rate, among others (KHAJAVI; ABBASIPOUR, 2017).

Ahn and collaborators (2006) produced Nylon 6 electrospun nanofibers for air filtration using the electrospinning technique. Their fibers ranged between 80 to 200 nm in diameter with a collection efficiency of 99,993% against 300 nm particles, at a velocity of 5 cm s^{-1} (AHN *et al.*, 2006). Matulevicius and co-workers (2014) produced polyamide (PA) nanofibers and observed spider-net shapes' formation during electrospinning. This nanostructure can improve the mechanical properties of PA mats (BARAKAT *et al.*, 2009) and can offer additional advantages to air filtration. The denser structure formed a layer capable of retaining more particles by interception mechanisms, raising the overall filtration efficacy. Single fibers sizes were around 465 nm in height and 220 nm in width. Spider-net structures ranged between 9-28 nm and 7-15 nm in height and width, respectively.

Nanofibers Filtering Efficiency: Nanofibers have already successfully captured viral particles, removing them from the air. Li and co-workers (2009) tested alumina nanofibers against aerosolized viruses' particles using MS2 bacteriophages. They observed low-pressure drops compared with HEPA filters, with high removal performance (LI *et al.*, 2009).

Electrospun nanofibers have excellent properties that enable the capture of efficient ultrafine particles (BONFIM *et al.*, 2021a; ZHANG *et al.*, 2017). Some of them are a large surface-area-to-volume ratio, low basis weight, nanoporous structures, and uniform electrospun fibers (MATULEVICIUS *et al.*, 2014). Worth mentioning that it is a low-cost technique (Nam *et al.*, 2019). So, nanofibers can be applicable for high-performance filtering.

To test the performance of nanofibers against nanoparticles, Leung & Sun (2020) used sodium chloride aerosols ranging between 50-500 nm to simulate SARS-CoV-2. They tested different nanofiber diameters of electrospun polyvinylidene fluoride (PVDF). As mentioned previously, they observed that the collection efficiency tends to rise by reducing the fiber diameter. Nanofibers with average diameters of 525, 349, 191, and 84 nm presented collection efficiencies of 39.6, 45.3, 51.8, and 61.9%, respectively

Liang and co-workers (2019) produced transparent fibers utilizing thermoplastic polyurethane, aiming at industrial-scale production. The retention efficiency was 99.654 % for PM 2.5, keeping the optical transparency of the filter at 60 %. After ten filtration cycles, the collection efficiency decreased only 1.6 % (LIANG *et al.*, 2019).

Bonfim and co-workers (2021) dissolved polyethylene terephthalate (PET) from clear soda bottles to produce nanofibers. They varied parameters such as solution concentration (10, 12, and 20 %) and needle diameter (0.3 to 0.7 mm), observing the response on structural characteristics of the electrospun fibers. The conclusion was that the fiber diameter suffers more influence from the concentration, thickening the fiber size with increased polymer content on the solution. It was also observed that the electrospun fiber of PET 20% had the lowest filtration efficiency (41%) for particles ranging between 7 to 300 nm. Polymer solutions with high concentrations tend to form thicker fibers, less effective in collecting nanoparticles. The electrospun fiber of less concentrated solutions (PET 10 and 12%) presents good collection efficiency, higher than 99% (BONFIM *et al.*, 2021b).

Fibers Functionalization: The fine particulate matter could also include a significant amount of viruses, bacteria, and fungi present in the air (DOWES *et al.*, 2003; FUNG; HUGHSON, 2003; SIDHESWARAN *et al.*, 2012). When used for long periods, air filters are susceptible to contamination (HAN *et al.*, 2019; YOON *et al.*, 2016). Hence, the fibers must also be highly active against microbes (JEONG *et al.*, 2007). A viable option to do this is functionalizing the filters with biocidal agents. Victor and co-workers used electrospun nanofibers of polyvinylidene fluoride (PVDF) with titanium nanotubes to purify air contaminated with bacteria. They observed that the blend could eliminate 99.88 % of the airborne microorganisms (VICTOR *et al.*, 2021). The biocide agent can be both organic or inorganic compounds, with different routes of inhibition of microbes (KALYON; OLGUN, 2001). Metallic nanoparticles are a common functionalizing agent, such as silver (NATEGHI; SHATERI-KHALILABAD, 2015; RAJABOOPATHI; THAMBIDURAI, 2018), copper (HUANG *et al.*, 2020; ZHAO *et al.*, 2020), and titanium. They have already proved effective against SARS-CoV-2 (ALLAWADHI *et al.*, 2021; JEREMIAH *et al.*, 2020; VAN DOREMALEN *et al.*, 2020) and other airborne microorganisms.

Machry and colleagues (2021) synthesized copper nanoparticles (CuNPs) to functionalize polyester fiber filters. Contact methodology was used to avail the bactericidal effect of the filters, proving excellent effectivity. Bacterial growth inhibition was more expressive in gram-positive bacteria (*Staphylococcus aureus*) than gram-negative (*Escherichia coli*) (MACHRY *et al.*, 2021). The proper mechanism is not entirely understood but indicates that CuNPs are responsible for producing Reactive Oxygen Species (ROS) that react with the outer layer of bacteria, leading to cell lysis and death (KEHRER, 2000; TOP; ÜLKÜ, 2004). Balagna and co-workers (2020) report that the use of silver nanocluster/silica composite sputtered coating applied on FFP3 masks possessed a virucidal effect against the coronavirus. They also clarify that the nanocluster can be applied to other surfaces like metals, ceramics, glasses, and polymers. Metallic oxides have also been investigated (MALLAKPOUR *et al.*, 2021).

However, the time required for the biocide action of inorganic materials is longer when compared with organic compounds (TOP; ÜLKÜ, 2004). Metal nanoparticles have cytotoxic effects on mammalian cells (LANONE; BOCZKOWSKI, 2006; TAVAKOLIAN *et al.*, 2020) and may harm the environment (EL-RAFIE *et al.*, 2014). To avoid side effects is recommended the usage of more natural compounds (EMAM, 2019). Many organic compounds are viable to confer biocidal action to textiles, such as Essential oils (ALONSO *et al.*, 2010; DAS, S. *et al.*, 2020; GONÇALVES *et al.*, 2020; PYANKOV *et al.*, 2012), cyclodextrins (LI *et al.*, 2014), triclosan (GOLJA *et al.*, 2016; ORHAN *et al.*, 2007), chitosan (FERNANDEZ-SAIZ *et al.*, 2009; LI; ZHUANG, 2020), and surfactants such as sodium dodecyl sulfate (SOUSA *et al.*, 2019) and cetyltrimethylammonium bromide (RAMESH *et al.*, 2003; SIMÕES *et al.*, 2008). The applications and mechanisms of surfactants as biocide agents are explored in the next section.

SURFACTANTS AND THEIR BIOCIDAL ACTIVITIES

Surfactants are common substances found in a series of different applications. It is present in various products such as toothpaste, mouthwash, shampoos, and detergents (HOWETT *et al.*, 1999). Typically, surfactants are not harmful to the skin and mucous (PIRET *et al.*, 2002) and may exhibit microbiocidal activity (FALK, 2019).

The word "surfactant" is an abbreviation of "surface active agent" because they are molecules able to diminish liquids' surface tension. Surfactants are a class of amphiphilic organic substances, having a hydrophobic group in one part of the molecule and a hydrophilic group in the other, usually called *tails* and *heads*, respectively (DAVIDOVITS, 2019). Surfactants can modify particle-surface interactions and provide a steric barrier to contact. Adsorption of their molecules can alter a series of interfacial properties such as van der Waals forces, electrostatic attraction and, hydrophobicity (FREE, 2016).

The surfactants can be classified into four significant groups: cationic, anionic, amphoteric, and non-ionic (FALK, 2019; NAKAMA, 2017). Anionic surfactants comprise molecules with an anion at the hydrophilic head, while cationic (usually quaternary ammonium bases) have a positive functional group (cation). Non-ionic surfactants are constituted by molecules that did not undergo ionization during dissolution (VAN OSS, 2008), and amphoteric surfactants possess both cationic and anionic surfactants.

The presence of hydrophobicity and positive charges in biocides agents are excellent characteristics for their antimicrobial activity (LIN *et al.*, 2002). Bacteria have an outer lipid-protein layer composed of lipopolysaccharides, giving the cell a negative charge (KOZIRÓG *et al.*, 2019). Strong electrostatic attraction between a cell membrane and biocide is favorable for biocidal action (NECHITA *et al.*, 2015). Biomolecules interact with ionic surfactants leading to denaturation and biological activity decay (CHATTOPADHYAY *et al.*, 2002). Non-ionic surfactants have weak action to denature proteins since they cannot correctly bind themselves to biomolecules (MAKINO; NIKI, 1977; TAWFIK *et al.*, 2015).

Amongst the cationic surfactants, the quaternary ammonium compounds (QAC) exhibit a good interaction with microorganisms. The hydrophobic tail of quaternary ammonium salts can penetrate the hydrophobic microorganism membrane core, leading to structural proteins and enzyme denaturation (EMAM, 2019). For example, gemini surfactants show good effectiveness against bacteria and microscopic fungi due to their molecules' high positivity (KOZIRÓG *et al.*, 2019). The alkyl groups' compounds that present a length chain between 12-14 exhibit better activity against Gram-positive bacterial strains. Compounds with 14-16 alkyl groups favor biocidal action against Gram-negative strains (GILBERT; MOORE, 2005). The surfactant action begins by penetrating

its molecules into the cell wall, reaching and reacting with the cytoplasmatic membrane. The intracellular matrix of bacteria is destabilized by the ion exchange of QAC with Ca^{2+} and Mg^{2+} from the cytoplasmatic membrane (TAVAKOLIAN *et al.*, 2020). The intracellular material is leaked, leading to proteins and nucleic acid degradation. As a consequence, the cell suffers lysis and death (MCDONNELL, 2007).

Some bacteria are surrounded by a capsule and slime that accumulate outside the cell wall. These secreted materials are responsible for the significant bacterial insusceptibility of biocides (MAILLARD, 2002). The spore's coat proteins act as an outer barrier, making the biocide's entrance challenging (PERMPOONPATTANA *et al.*, 2013). Some Gram-positive bacteria form spores as an additional defense (FALK, 2019; KABORÉ *et al.*, 2019). Gram-negative cells also have a supplementary barrier, an outer membrane, which Gram-positive cells do not have. This lipopolysaccharide layer after the polypeptidoglycan wall also difficult the biocide penetration (DENYER, 1995). One way to avoid those barriers is by combining different biocides to improve the biocidal action (DENYER, 1990). The use of EDTA (ethylenediaminetetraacetic acid) as a secondary agent, for example, raises the permeability of the cell wall, allowing a primary biocide to get closer to the cell membrane (MAILLARD, 2002).

Fungi and yeasts can also be affected by cationic surfactants' antimicrobial activity (BONVILA *et al.*, 2008), reducing the number of fungal spores (KOZIRÓG *et al.*, 2019). Surfactants act by dispersing the fungi aggregates, influencing their surface structure, and changing the fungal surface's physicochemical properties of the adsorption process (HAMZAH *et al.*, 2018). The hydrophobic portion of the surfactant coats the fungal surface, also hydrophobic. The other part of the surfactant molecule is exposed to the ambient, giving hydrophilic properties to the fungus outer layer (WU; PENDLETON, 2001). This effect, combined with the electrostatic adsorption phenomenon at the water/membrane interface, disrupts the fungi surface structure (WU *et al.*, 2019), causing its death.

Some surfactants also present antiviral properties, and their presence decreases viruses' survivability (CHATTOPADHYAY *et al.*, 2002). The inactivation of viruses under surfactants was already studied with HIV (human immunodeficiency virus) (SOUSA *et al.*, 2019), Ebola (CHEPURNOV *et al.*, 2003), and H1N1 flu (NUMATA *et al.*, 2020), for example. They have shown a good inhibition effect, acting against enveloped and nonenveloped viruses. The mechanism involves the denaturation of

proteins in the viral capsid and dissociates the viral envelope (SOUSA *et al.*, 2019). Surfactants can also denature and unfold monomeric and subunit proteins (HOWETT *et al.*, 1999) and form micelles around the capsid or membrane, enclosing the virus (PRAMOD *et al.*, 2020). They also diminish viruses' sorption and consequently increase their mobility (CHATTOPADHYAY *et al.*, 2002).

Surfactants also have a role in the recent pandemic and can be a good option against the SARS-CoV-2 virus. The inactivation by surfactants occurs through damage in their spikes (STURMAN *et al.*, 1990). Surfactants can also act *in situ* by reaching cells and extracellular fluids interfering in one or more steps of viral replication (PRAMOD *et al.*, 2020). The human body has natural surfactants working on defense against the new coronavirus-2019. Our systems produce a protein surfactants monolayer to control the interface air-epithelium of lung alveoli (LETH-LARSEN *et al.*, 2007). The objective is to reduce surface tension at the end of expiration, avoiding the lung alveoli's collapse (HAWGOOD; CLEMENTS, 1990). SARS-CoV-2 causes the inhibition of those natural surfactants (TAKANO, 2020), exposing the alveoli during the inhalation-expiration process.

The study performed by de Almeida *et al.* (2020) aimed to evaluate the filtration efficiency of cellulose acetate with cetyl pyridinium bromide, a cationic surfactant (and a quaternary ammonia salt). The authors found about 99 % efficiency for small particles for low surface air velocity, ranging from 7 to 300 nm. They also suggest that these nanofibers present biocide action (ALMEIDA *et al.*, 2020). Another study conducted by Jeong & co-workers (2007) prepared polyurethane cationomer nanofibers (PUC), using a mixture of QAC on its non-woven mats for antimicrobial nanofilter applications. They tested the sample's antimicrobial activity with low content of quaternary ammonium compounds against *S. aureus* and *E. coli*. The results showed a reduction of colonies in 99.9% after 24 h incubation (JEONG *et al.*, 2007). They also observed that the fiber diameter of electrospun PUC decreases with increasing the quaternary ammonium group content.

Zhang *et al.* (2020) produced a nanofiber mat of PVA (polyvinyl alcohol), functionalizing with a quaternary ammonium salt and zwitterionic sulfopropylbetaine. They observed that only 0.5% of surfactant applied to the fibers could achieve 99.9% antimicrobial activity against *S. aureus* and *E. coli* (ZHANG, T. *et al.*, 2020). It was much lower than the amount used in a previous research group study using cotton textiles

(ZHANG, S. *et al.*, 2018). This result is attributed to the higher surface area of PVA mats, and the bond between the quaternary ammonium salt and the PVA fiber is covalent instead of physical. The stronger bond avoids a loss of biocide agents and improves its durability. A different study also used sulfopropylbetaine (SSPB) for biocidal purposes. They functionalized cotton fabrics, observing that the addition of SSPB also improves the fabrics' mechanical resistance (CHEN *et al.*, 2011).

The presence of QAC in a membrane can also change the surface properties for other purposes. Researchers have functionalized a PVDF membrane with polydopamine and polyethylenimine to synthesize an outer layer of hydrophilic nanoparticles *in situ*. Then, the immobilized QAC on the silica layer produces an antibacterial layer. They observed that after adding QAC, the membrane gains biocidal activity. It also prevents biofouling, the adhesion of microorganisms on its surface, avoiding bacterial and fungal growth. They also tested the system's durability to wastewater treatment, obtaining 85% elimination for Gram-positive and Gram-negative bacteria after washing the filter for 9 hours (ZHANG, X. *et al.*, 2018).

HVAC'S & VENTILATION SYSTEMS

The recent pandemic has cast doubt on the reliability of ventilation and HVAC systems due to the mechanisms of the disease's spread through airborne droplets. Air conditioning could transfer respiratory droplets containing the virus to persons standing against the airflow direction (LU *et al.*, 2020). Those droplets can also travel inside the ventilation systems, disseminating the virus by being reinserted in the room, as already proved by modeling systems (SHAO *et al.*, 2021). There are proposed three routes of contamination (CORREIA *et al.*, 2020):

- Through air recirculation in the buildings;
- Through the ventilation exhaustion;
- Through air confinement, without renewing the ambient with fresh air.

There are many suggestions to avoid those problems, such as improving ventilation rates, adopting natural ventilation and, personalized ventilation and exhaustion systems for micro-environments (QIAN; ZHENG, 2018). The pivotal advice

is to increase outdoor air in ventilation systems and keep the system running day and night (GUO *et al.*, 2020). On the other hand, the American Society of Heating, Refrigeration, and Air-Conditioning Engineers (ASHRAE) positioned against the advice of not running HVAC systems and defending that air conditioners can help contain the spread of the virus (SHERRI, 2020).

Nevertheless, some situations cannot adapt to the last changes proposed. For example, natural ventilation is not easy to implement in the middle east, with extremely high temperatures (38 to 42 °C) (AMOATEY *et al.*, 2020). The buildings' architectural design did not allow natural and mechanical ventilation, constructed with indoor air conditioning systems to maintain thermal comfort (ALJOFI, 2016). The dependence on ventilation and HVAC systems also increases in the occident. With temperature rises, global warming, and heat waves happening more frequently and persistently worldwide (LI, 2020), the necessity for air conditioning and improvements in ventilation systems only tends to rise.

There are other roles that ventilation systems can play against pathogens. When the airflow passage is blocked, there is a risk of increasing the airborne pathogens' concentration and growth, increasing the chances of airborne pathogens' transmissibility (GILKESON *et al.*, 2013). Ventilation systems can withdraw respiratory droplets from the room three times faster than natural ventilation (LYNCH; GORING, 2020), removing exhaled virus-laden air and diminishing the virus concentration (CORREIA *et al.*, 2020; MORAWSKA *et al.*, 2020). They are also effective in eliminating airborne bacterial and fungal spores (KUJUNDZIC *et al.*, 2006). Air cleaners also reduce aerosolized virus concentration, especially when adopted alongside natural ventilation (LEE *et al.*, 2021). A possible improvement to ventilation, heating, and HVAC systems is air filters. HEPA's implementation can help control the spreading in facilities with common ducts (SHAKOOR *et al.*, 2015). Air viral particles' extraction was already observed in an airplane with HEPA in its ventilation systems (MAZUMDAR; CHEN, 2009). Air recirculation also reduces infection risk in areas sharing the same central HVAC system (CORREIA *et al.*, 2020).

CONCLUSION

Due to the growing number of studies under development in recent years, we believe that soon there will be a range of innovative products composed of specialized materials as filter media. Incorporating biocidal and virucidal compounds in commercial filters/textiles and filtering nanofibers is an effective alternative to keep indoor environments safe from nanoparticles and pathogenic organisms. Surfactants are eco-friendly compounds, unlike the metallic nanoparticles widely used today. Thus, being a compound not harmful to human health, its use will occur through its incorporation into microcapsules with controlled release in textiles and nanofibers for masks and various articles for health professionals. Also, considering the control of indoor air pollution, its addition in solution for producing electrospinning nanofibers has already proven effective in inactivating several pathogens, such as viruses and bacteria.

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