Mesoporous Silica Adsorbed on Cellulosic Textiles with Strong Antibacterial Properties against Foodborne Pathogens

Elnawawy, A. S.[1]; Khalil, M. S.[2]; Molins, E.[3]; Benito, M.[3]; Rodríguez-Jerez, J.J.[4] and Guerrero, A.[4]

[1]*Food Engineering and Packaging Department (FEPD), Food Technology Research Institute (FTRI), Agriculture Research Center (ARC), Giza, Egypt.*

[2]*Department of Botany and Microbiology, Faculty of Science, Cairo University (CU), Giza, Egypt.*

[3]*Departamento of Cristalografía, Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, Barcelona, España.*

[4]*Departamento de Ciencia animal y de los alimentos, Facultad de Veterinaria, Campus de la UAB, Barcelona, España.*

ABSTRACT

Low density - highly porous tetraethoxysilane (TEOS) - based silica aerogels and cryogels were prepared in acidic water via a one-step process. The approximate values of the average pore diameter are 13 and 9 nm, and BET surface areas are 881 and 723 m^2/g for aerogel and cryogel films, respectively. The silica films shrinkage related to drying was largely reduced because the sol-gel was adsorbed on gauze and non woven textiles. Supercritically dried films are compared with cryogels, also through optical properties, Scanning Electron Microscopy (SEM) and Attenuated Total Reflection -Fourier Transform Infrared Spectroscopy (ATR-FTIR).

Based on ISO 22196:2007, the antibacterial activity of the untreated and antibacterials-treated cryogel silica films adsorbed on gauze textile were evaluated. Both films showed strong antibacterial properties against the food pathogens *Escherichia coli*, *Salmonella typhimurium*, and *Listeria monocytogenes*.

Keywords: *Aerogel, Active Packaging, Cryogel, SEM, Silica.*

I. INTRODUCTION

The consumers demand for safety and quality of food products is gaining significant attention from the scientists all over the world, due to human health and environmental concerns. Beside the increase of consumer desire for natural and organic products; these creates new challenges in providing efficient food preservation, especially in the area of microbial safety [1-3]. At the same time, many current methods for maintaining and enhancing food quality and safety do not satisfy consumers' demand; therefore, food industry has begun exploring alternatives to the present used chemicals. Several natural-source substances, including food packaging materials and antimicrobials, had proven effective in laboratory settings [4-6]. Addition of food preservatives directly into food is an established practice with some disadvantages. Instant addition of antimicrobials in formulation often results in instant inhibition of non-desired microorganisms; but the survivors will continue to grow especially when antimicrobials added by formulation will get depleted. This may happened due to complex interactions with the food matrix or by natural degradation over time causing short shelf-life [7-9].In addition, gradual decrease in antimicrobials concentration may lead to development of the antimicrobial-resistant mutants [7]. To overcome these disadvantages, new

technologies, namely "Active Packaging" used to extend the product's quality, safety and shelf life **[10-12]**. The scientific progress in packaging technologies allows materials to do more than just encompass the food. Antimicrobial packaging is a promising form of active packaging to improve safety and shelf-life of food products **[10, 11]**; whereas edible films can be used to replace traditional packaging and they could be an alternative for synthetic films **[13, 14]**.

Silica comes next to oxygen in abundance in the Earth's crust; it is present in the form of silicate minerals. It is already used in consumer products, mainly cosmetics, pharmaceuticals and foods. Silica oxide is present in soils, in some plants and in some organisms such as diatoms. Silica is also a natural element found in foods such as in grains, especially oats, barley and in some rice fractions **[15]**. It is incorporated into a variety of food products for the clearing of beverages, and mostly as anticaking agent, stabilizer, carrier and emulsifying agent in many powdered food products.

Synthetic amorphous silica is also used for surface coating of packaging materials **[16,17]**; it used in the pharmaceuticals, as carrier for various drugs and vitamin**s [18]**.   It is considered a safe excipient in pharmaceutical drugs, based on the reports from FDA **[19]**, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) **[20]** and European Union **[21]**. These reports confirm the safety of silicates and provide further support that silica is Generally Regarded as Safe (GRAS) when added either directly or indirectly to food; therefore, silica containing films can be considered edible.

Preparations of several materials for different applications by using the supercritical drying aerogel and freeze drying cryogel techniques have received considerable attention in recent years **[22-30]**.The preparation of mesoporous silica film can be achieved by both using supercritical fluids (aerogels) **[31, 32]**and freeze drying (cryogels) **[22, 27]** techniques. Aerogels and cryogels are nano scale mesoporous light materials, possessing a number of exceptional physical and chemical properties. These attract the attention of researchers in various areas of science and technology **[33-40]**.They usually present large surface areas (500–1500 m^2/g), high porosity (80–99%) and low densities (0.03 – 0.3 g/cm^3) **[27,41-44]**. **Kistler [45]** was the first who discovered "Aerogels", which applied the supercritical drying technique, in which the liquid inside the gel pores was transformed into a supercritical fluid; so the liquid was replaced with a gas without collapsing the gel pores. The term "cryogel", was first introduced in the medicine; it is widely used in the preparation of a sticky gelatinous fraction of the blood plasma that associated with several specific kinds of diseases **[46, 47]**. In general, the supercritical fluids have a high solvating power and almost zero surface tension. These make them ideal for the removal of solvents from wet gels; while avoiding the surface tension force associated with the removal of the solvent by the ambient pressure **[48, 49]**. Low temperature supercritical drying (LTSCD), is a method for aerogel drying which was suggested by **Tewari *et al.* [50]**. The solvent present in the gel before drying (generally alcohol) is replaced by liquid CO_2, because it has a critical point close to ambient temperature **[51]**. Low temperature supercritical drying has the advantage of being implemented at a low temperature (<40 ℃) and moderate pressure (<80 bar) **[52]**. For cryogels, they are obtained by freezing gels and then sublimed under vacuum **[53]**. The main problem with this technique is that the nucleation and growth of solvent crystals destroy the gel network, producing large pores **[54]**. This problem was solved by using solvents with a low expansion coefficient, a high sublimation pressure and the flash freezing of the samples by using liquid nitrogen **[55]**; so the small crystals are then nucleated. Cryogel silica dioxide powders

with a texture close to those of aerogels were obtained using this technique by **Hyun *et al.* [56]** and **Pajonk *et al.* [57]**. Food packages can be made "antimicrobial" by immobilizing antimicrobial compounds into the packaging film **[10, 58-60]**. Silica nano particles exhibited remarkable impact on the fabrication and quality of antimicrobial casted films **[61, 62]**.

The aim of this research is to prepare aerogel and cryogel silica films by using one step procedure, followed by immobilizing bioactive antibacterial compounds into the suitable film; that can be commercially applied as antibacterial food packaging film.

II. MATERIALS AND METHODS

2.1. Materials

Tetraethyl orthosilicate (TEOS) 98%; Sigma-Aldrich. Gauze fabric, made from cotton, Hartman, Medicomp, Germany. Airlaid pulp non-woven textile from a local supplier market, Italy. *Tert*-butanol, ACS reagent, ≥99%, Sigma-Aldrich. Absolute Ethanol, 99.9% (UV-IR-HPLC), Panreac. Ammonium hydroxide solution, ACS reagent, 28.0-30.0% NH_3 basis, Sigma-Aldrich.   Acetic acid, ACS reagent, ≥99.7%, Sigma-Aldrich. Laboratory prepared mixture of antibacterial compounds: **(**Decane, 2,3,5,8-tetramethyl-**)**, **(**α-N-Normethadol**)**, **(**Pregnan-20-one, 3,11-dihydroxy-, (3β,5α,11β)-**)**, **(**Benzenepropanoic acid, 3,5-bis **(**1,1-dimethylethyl)-4-hydroxy-, octadecyl**)**, **(**Quinoline, 2-phenyl**)**, **(**Pyridine, 2,4,6-triphenyl-**)** and (Pyridine, 2-methyl-3,4,5,6-tetraphenyl-**)**.

2.2. Methods

2.2.1. Preparation of silica aerogel and cryogel

Silica sol-gel was synthesized by using one step acid catalyzed procedure innovated by the author. 0.06 mol of TEOS was hydrolyzed with Milli-Q water acidified with glacial acetic acid; the resulted transparent and homogeneous solution was adsorbed on gauze and non-woven textiles beside the free films; all the samples kept up to gelation take place. The samples were divided into two; a group for supercritical CO_2 drying and group for freeze drying in which absolute ethanol and *tert*-butanol were used as washing solvents respectively.   For the first washing time, ammonium hydroxide was added to the washing solvents to neutralize the acetic acid in the gels.

Supercritical and freeze drying process were carried out in order to obtain aerogels and cryogels respectively. For aerogel silica, the gel was dried by low temperature supercritical drying (LTSCD) **[52]**, which was performed in a homemade SCF 300 ml plant in the supercritical fluids Lab. For cryogel silica, the gel was dried by using the LyoQuest-80 freeze dryer from Telstar working at 0.05 mbar and -85 ºC.

2.2.2. Characterization methods

2.2.2.1.   Weight of adsorbed Silica on the textiles pieces

The amount of adsorbed silica on the textiles for both the aerogel and cryogel films was weighted; each value represents the average weight of two pieces for each film sample. Measurements for the pure textiles without silica were determined as control samples.

2.2.2.2. Viscosity

Viscosity of the silica sol gel was measured using Brookfield Engineering labs DVIII Ultra Rheometer. The sample was placed in a small sample adaptor at room temperature (~21°C), and measured at 50 rpm in duplicate by using the SC4-21 spindle.

2.2.2.3. Optical properties

Optical properties of aerogel and cryogel silica films, obtained after drying were visually determined by using black and white backgrounds.

2.2.2.4. Scanning Electron Microscope (SEM)

The morphological characteristics for the films were examined with two different scanning electron microscopes (SEM). The surface characteristics and pores shape for both the aerogel and cryogel free silica films were examined using the scanning electron microscope (SEM) FEI Quanta FEG 650; while the samples coated with Platinum layer (5-10nm in thickness). Aerogel and cryogel SiO_2 films adsorbed in textiles pieces were analyzed with the scanning electron microscope (SEM) QUANTA FEI 200 FEG-ESEM.

2.2.2.5. Specific Surface Area (SSA)

The specific surface area, adsorption average pore width and pore diameter, and desorption average pore diameter for aerogel and cryogel samples were analyzed by nitrogen adsorption measurements using a surface area and porosimetry analyzer (Micromeritics ASAP 2000). Nitrogen adsorption and desorption isotherms were measured at 77 K on a Micromeritics ASAP 2000 analyzer. All the samples were out gassed at 373 K for 4 h prior to the nitrogen adsorption measurements. The specific surface area was calculated by the BET method. The pore size distributions were obtained from the adsorption and desorption branch of the nitrogen isotherms by the Barrett-Joyner-Halenda method.

2.2.2.6. Attenuated Total Reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR)

Aerogel and cryogel free silica films and for those adsorbed on the textiles pieces were characterized by Attenuated Total Reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR) analysis using a PERKIN ELMER Spectrum one spectrophotometer. The device equipped with U-ATR (Universal Attenuated Total Reflection) accessory. Spectra were collected within the range of 4000 – 600 cm^{-1}, at a resolution of 4 cm^{-1} for 8 scans.

2.2.3. Application

2.2.3.1. Immobilization of bioactive compounds and antibacterial evaluation

Cryogel silica film adsorbed on the gauze textile was used for the antibacterial activity test. 1 mg and 500 ηg were used as two different concentrations of the antibacterial compounds mixture that was laboratory prepared and evaluated [63]. Gauze pieces adsorbed with silica film were used as positive control, and pure gauze used as negative control. The antibacterial compounds mixture loaded on the gauze pieces before drying. The antibacterial activity of the films was developed based on the ISO standard: ISO 22196:2007 by using *Escherichia coli* ATCC 10536, *Salmonella enterica subsp. enterica serov typhymurium* CECT 722 and *Listeria monocytogenes* CECT 935. Detection of bacterial cells counts was preceded by using the bioMerieux TEMPO^R system. The test was performed on three replicates per test species of the treated test material to reduce variability. The results analyzed statistically by using ANOVA test.

III. RESULTS AND DISCUSSION

In this work, we succeed to prepare natural films that can be used in food packaging. The antibacterial silica film containing intact mesopores prepared by immobilizing previously prepared antibacterial compounds **[63]**. The purpose of using the aerogel and cryogel techniques is maintaining the pores formed inside the sol-gel due to the polymerization of the film components. Because upon solvent removal by traditional drying procedures, e.g. ambient air drying, the surface tension of the liquid contained in the gel nanopores infer a capillary pressure gradient in the pore walls reaching pressures of up to 100–200 MPa, able to collapse the pores **[31, 32, 52, 64]**. In supercritical drying method, the pores liquid was removed above the critical temperature (T_c) and critical pressure (P_c) of the concerned liquid. At this point there is no liquid–vapour interface and thus no capillary pressure [**65**]; at the end of this process we obtained the aerogel silica film. In the freeze drying method, problems due to the surface tension were avoided by freezing the wet gel and then extracting the solvent by sublimation [**65, 66**]. The pores liquid exchanged with a low expansion coefficient and a high sublimation pressure under vacuum [**67**]; to obtain the cryogel silica film. A significant amount of work has been carried out in the field of both silica cryogels **[68-71]** and aerogels **[72-77]**. The silica sol-gel was prepared by a new synthesis method by dissolving TEOS in acidified water through one step procedure.   Both aerogel and cryogel films were prepared for the purpose of comparison between both of them; and then choose the one that can be used as a carrier of the antibacterial compounds.   It is well known that, hydrolysis of silicon alkoxide is a versatile technique which can yield different products according to different parameters and acid or base catalysis reaction. The proportion of TEOS and water is considered a critical point in the preparation of the sol gel **[78]**. As water and alkoxysilane TEOS are partially immiscible, additional solvent is needed to homogenize the mixture; therefore acidic water was used as catalyst and hydrolyzing agent **[79]**. The gelation times are generally longer when the pH of the sol gel is low [**80**]. In this work, silica films remained stable without any shrink during the aging and washing steps. Both the aerogel and cryogel films were extremely brittle materials; shrinking of the gel network occurs after drying the films as shown in **Fig. (1)** against a dark background. For freeze-drying method, it is generally believed that cryogels can only be obtained as powders [**81, 82**]; but we obtained larger and more fracture resistant fragments and monoliths as shown in **Fig. (1)**. This is because, the type of solvent that replaces the original synthesis solvent affects the degree of monolithicity; water produced only powders while *tert*-butanol produced cryogels with a variable degree of monolithicity**[22]**.

The resulted aerogels and cryogels are rather transparent; because there is a small amount of scattering light in the visible. The scattered light has a relatively isotropic angular distribution, and exhibits little multiple scattering [**83-85**]. The results obtained after the drying step of the films compelled us to adsorb the film sol gel on cellulosic textiles as support; to help the preparation of aerogel and cryogel silica films that can be used as food packaging films. Low cost and easy available cellulosic fabrics were used as adsorbent for the silica sol. Gauze textile was used previously as adsorbent for natural polymers **[86-88]**, while this is the first time for using the non-woven textile as adsorbent **(Fig. 1)**.   The success of the adsorption of the silica film, which prepared by both the aerogel and

cryogel methods, proved firstly by the weight difference between the treated and untreated textiles as presented in **Table (1)**.

The viscosity of the sol (2cP) helped in its adsorption on the textiles. It is noticed that, the amount of silica adsorbed on non- woven textile is slightly higher than those adsorbed on gauze textile. This can be probably attributed to the internal structure of the textiles which illustrated by the Scanning Electron Microscopy (SEM) of the untreated pieces as shown in **Fig. 2 (c)** and **2 (d)**. As it can be observed, the cotton gauze is an open loose weave formed by cords leading to the formation of highly porous interconnected structures. Meanwhile the non woven textile used in this work consists of flat belts forming a more dense packed structure as shown below.
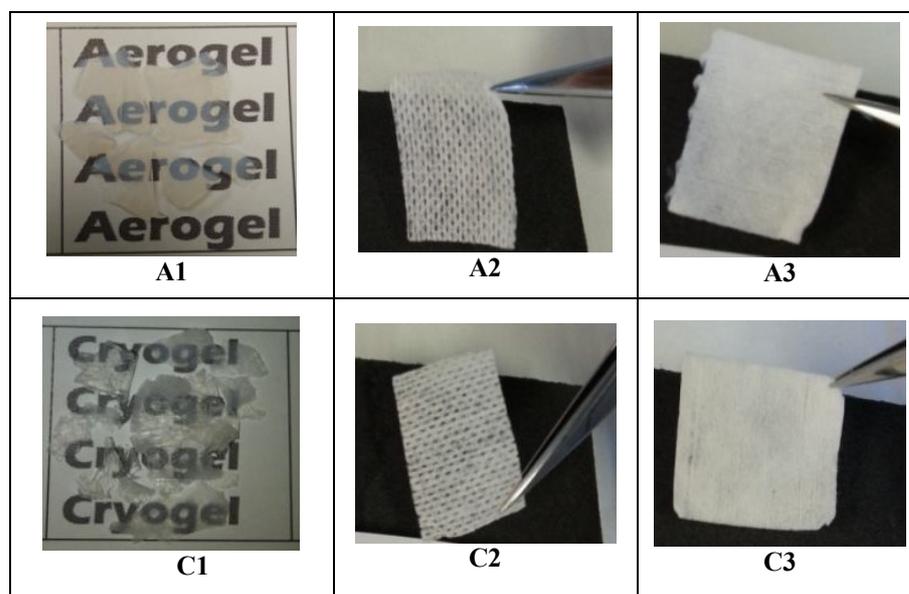

Fig (1).Photographs of SiO$_2$ films obtained for aerogels and cryogels: A1: aerogel SiO$_2$ film; **A2**: aerogel SiO$_2$ film on gauze; **A3**: aerogel SiO$_2$ film on non-woven; **C1**: cryogel SiO$_2$ film; **C2**: cryogel SiO$_2$ film on gauze; **C3**: cryogel SiO$_2$ film on non-woven

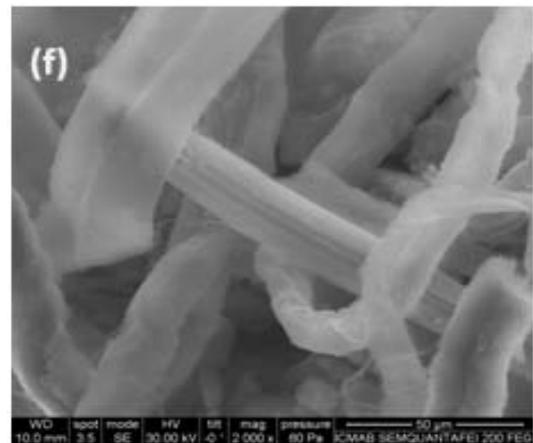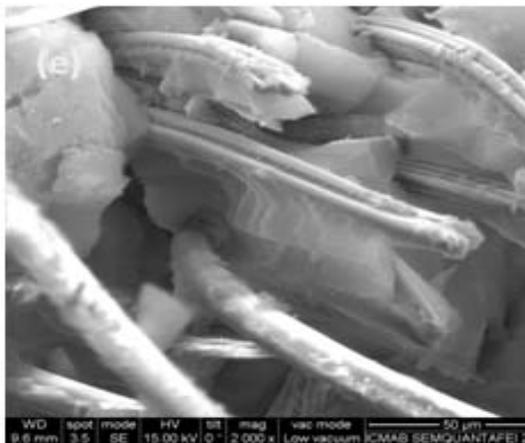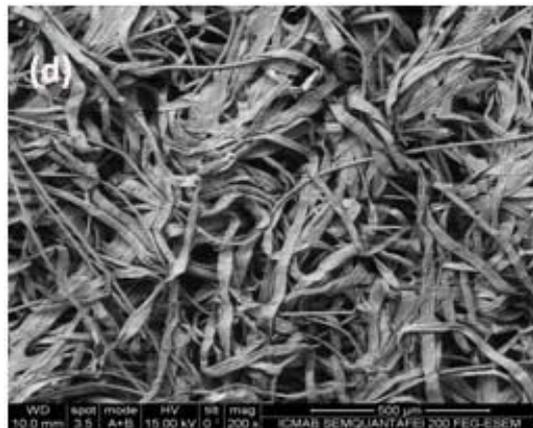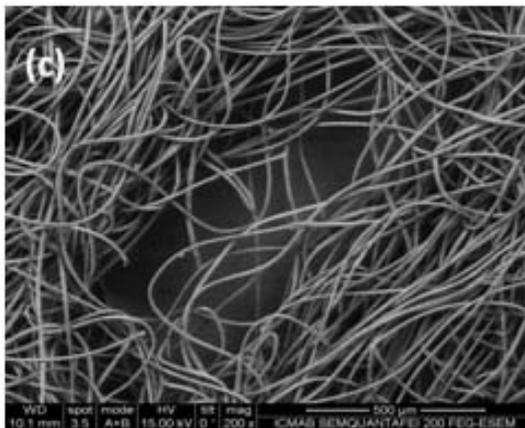**Table 1. Weights of adsorbed aerogel and cryogel SiO$_2$ on gauzes and non woven pieces**

Sample*	Amount of adsorbed Silica \g**
A2	0.020
A3	0.028
C2	0.023
C3	0.026

*Textile piecesize2cm × 2cm

**Weight difference between the pure textiles and the textiles adsorbed with the silica.

SEM images of aerogel and cryogel SiO$_2$ monoliths are shown in **Fig. 2(a)** and **2(b)**; both show sponge-like structure. However, particle and pore size for aerogel monolith are higher, increasing roughness. On the contrary, the silica cryogel monolith appears as a flatter surface with a narrower pore size. SEM micrographs of aerogel and

cryogel silica films adsorbed on the textiles are shown in **Fig. 2(e), 2(f), 2(g)** and **2(h)**; silica is completely covering the inner and outer surface of both textiles. The good strength of adsorbance to the gauze and non woven textile is demonstrated. Although the cryogel samples seem to be more cracked; maybe as a consequence of SEM preparation.
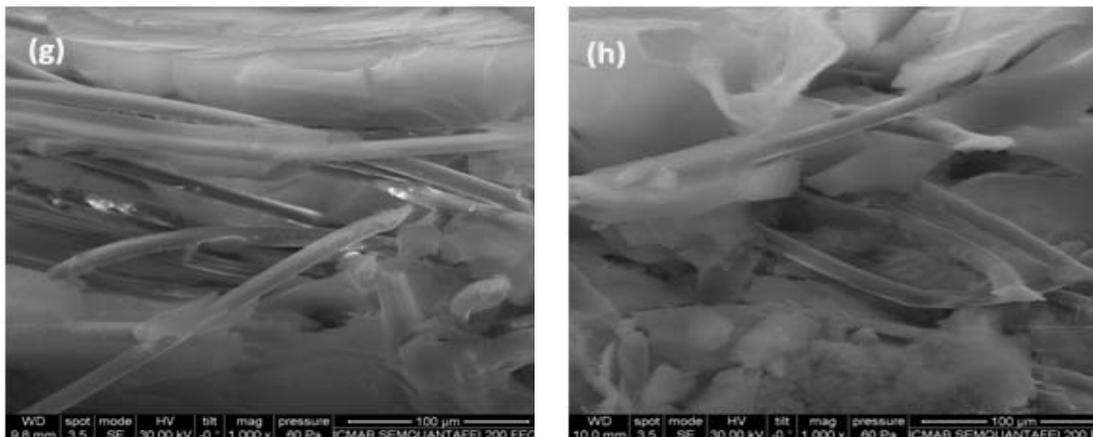
Fig (2). Scanning Electron Microscopy (SEM) micrographs of silica films: (a) A1 (mag:100000X), (b) C1 (mag:100000X), (c) Untreated gauze (mag: 200X), (d) untreated non-woven (mag:200X), (e) A2 (mag: 2000X), (f) A3 (mag:2000X), (g) C2 (mag:1000X) and (h) C3 (mag:1000X).

The specific surface areas of all aerogels and cryogels samples are summarized in **Table (2)** using the BET method. It is considered the most widely utilized method for determination of aerogel and cryogel porosity by using nitrogen adsorption/desorption technique or BET method **[89-91]**. In this method, the amount adsorbed nitrogen gas is measured to coarsely distinguish various pore shapes by the type of isotherms **[92]**. Pure silica aerogel and cryogel films show high specific surface areas in the range 700-900 m^2/g being the corresponding to the aerogel higher than the cryogel, 881 m^2/g *vs* 723 m^2/g. Although the values for specific surface areas of SiO_2 adsorbed on textile materials are lower than for free monoliths, the same trend is observed.

Table 2: Specific Surface Area (SSA) for the aerogel and cryogel silica dioxide films

Sample	BET Surface Area* m^2/g	Adsorption average pore width (4V/A by BET)\ nm	BJH Adsorption average pore diameter (4V/A)\ nm	BJH Desorption average pore diameter (4V/A)\ nm
A1	881	13	13	12
C1	723	10	9	8
A2	406	12	18	16
C2	327	13	12	12
A3	481	13	17	15
C3	363	15	15	14

* Micropore surface area **(Dubinin-Radushkevich)** for pure gauze (0.0129 g) = 168112852.516504 m^2/g

Micropore surface area **(Dubinin-Radushkevich)** for pure non-woven (0.0201 g) =0.019812 m^2/g

However, it is interesting to remark the higher SSA value for the non -woven fabrics in both cases for aerogel (481 m^2/g) and cryogel (363 m^2/g) preparations. This is probably because of the more compacted network of the non woven textile, its higher ability to retain a bigger amount of silica as observed in **Table (1)** and the smaller particle

size as a consequence of the drying process. According to IUPAC classification for porous materials, the pores less than 2 nm in diameter are termed "micropores"; those with diameters between 2 and 50 nm are termed " mesopores" and those greater than 50 nm in diameter are termed "macropores"[93]. The average pore diameters of all the samples were in the range of 9 – 18 nm, so in the mesoporous range **(Table 2)**.

Comparison of average pore width and average pore diameter distributions between the resulted aerogel and cryogel silica films, as illustrated in **Table (2)**, indicates several aspects. The pore diameter tends to be larger and pore width tends to be wider for aerogel than the cryogel silica film. These results are conflicting to that found by **Pons *et al.*,[22]** and others; which were obtained larger and wider pore sizes for cryogels than for aerogels silica.

On the other hand, by comparing the average pore width and average pore diameter distributions among the resulted textiles adsorbed with aerogel and cryogel silica films, the results changed. These may be attributed to the effect of the textiles on the formation of the chemical bonds during the aging of the samples. These chemical bonds investigated by the Attenuated Total Reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR), as shown in **Fig. (3)** and **Table (3)**.
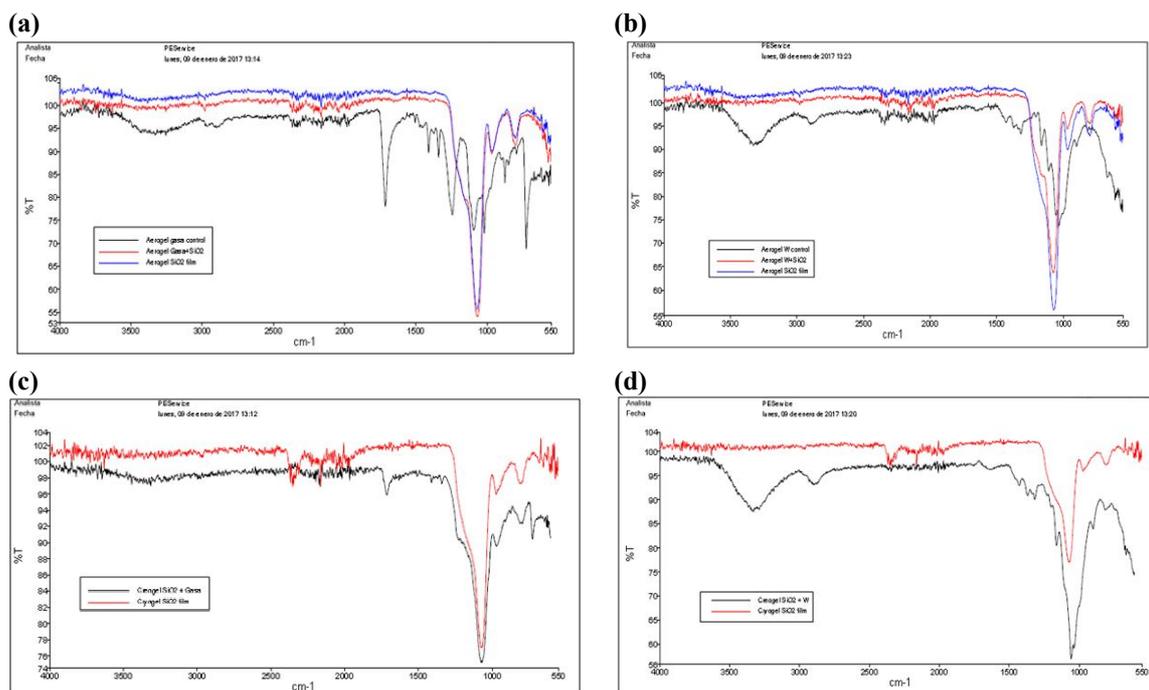

Fig (3): ATR-FTIR spectra of (a) untreated gauze, A2 and A1 ,(b)Untreated non-woven, A3 and A1, (c) C2 and C1 and (d)C3 and C1.

The ATR-FTIR spectra of the silica aerogels and cryogel films are shown in **Fig (3)**. The analysis of the common bands of each spectra revealed that, the intense silicon–oxygen covalent bonds (–Si-O-Si-) vibrations appears at the frequencies ranged between 791 cm^{-1} and 1159 cm^{-1} **[65, 94,95]**. This revealing the existence of a dense silica network; where oxygen atoms play the role of bridges between each two silicon sites as shown in **Fig.(5)**. The low energy bands are ranged between the frequencies 556 cm^{-1} and 591 cm^{-1}; they are assigned to Si-O stretching of the SiO_2 network defects **[65]**. The bands for the silanol polar group (Si-OH) appear at the frequencies ranged between

International Journal of Advance Research in Science and Engineering
Volume No.06, Issue No. 11, November 2017
www.ijarse.com

IJARSE
ISSN: 2319-8354

965 cm^{-1}and3361 cm^{-1}[96]. This group considered the main source of hydrophilicity, because they can promote the adsorption of water [52]. The transmission bands corresponding to the adsorbed water molecules deformation vibrations (H-O-H) appears only in the aerogel samples A1, A2 and A3, at the frequencies 1647 cm^{-1}, 1654 cm^{-1} and 1637 cm^{-1} respectively [97].

Table 3.Infrared absorption frequencies of silica films.

Assignments	IR absorption frequencies (cm^{-1})*						
	A1	A2	A3	C1	C2	C3	Literature**
SiO$_2$ defects	556 582 568 590	568 582 590	562 581 591	556 569 581			554-590[1]
-Si-O-Si- Antisym. Str.	798	798	798	807	791		798[1] 782-799[1] 782-805[1]
-Si-OH	964	964	965	970	969		964[2], 965[2], 969[3]
-Si-O-Si- Sym. Str.	1071	1066	1074	1073	1073	1034 1055 1159	1067-1095[4,5] 1000-1250[5,8] 1136-1200[4,5]
H-O-H	1647	1654	1637				1632-1654[6]
-Si-OH		3326		3361	3315	3330	3300-3370[7]
H-O-H….H$_2$O and -SiO-H.....H$_2$O		3458	3440				3450-3475[1]

   * **A1**: aerogel SiO$_2$ film; **A2**: aerogel SiO$_2$ film on gauze; **A3**: aerogel SiO$_2$ film on non-woven; **C1**: cryogel SiO$_2$ film;
   C2: cryogel SiO$_2$ film   on gauze; **C3**: cryogel SiO$_2$ film on non-woven
   ** **[1]**[65]; **[2]**[96] ; **[3]**[100]; **[4]**[94]; **[5]**[95]; **[6]**[97]; **[7]**[99]; **[8]**[101]

The adsorption of water molecules on the surface of the aerogel samples is due to the existence of the surface silanol groups, which responsible to the hydrophilic nature of the films [98].

The absence of water molecules in the cryogel samples although silanol groups exist on their surfaces can be attributed to the exposure of the aerogel samples to the laboratory atmosphere during the transfer of the samples from the device to the collected boxes, while the cryogel samples remained in their boxes.

The bands at frequencies at 3458 cm^{-1} and 3440 cm^{-1} correspond to the stretching bands of hydrogen-bonded water molecules (H-O-H….H$_2$O) and the SiOH stretching of surface silanols hydrogen-bonded to molecular water (SiO-H.....H$_2$O) [**65**].

Silica cryogel film adsorbed on gauze textile was selected for antibacterial compounds inclusion; a mixture of antibacterial compounds was immobilized into silica network. The bioactivity of this mixture has been previously investigated by **Elnawawy** *et al.,* [**63**]. Here we report silica cryogel film on gauze textile containing those antibacterials and its bioactivity against food pathogenic bacterial strains.   Although this film does not have the highest specific surface for maximum adsorption, its preparation by freeze drying is much more feasible from an industrial point of view. On the other hand, it is difficult to maintain the antibacterials immobilized on the film during the supercritical drying process.   Moreover, cotton gauze is a natural textile and it can be applied for food packaging. One important aspect of the cryogel pore network (also for aerogel) is its "open" nature and interconnectivity as illustrated in **Fig. (5)**.   In open-pore structures, fluids can flow from pore to pore, with limited restriction, and eventually travel through the entire material.   Therefore we suppose that, the nano sized antibacterial compounds may be encapsulated in those open pore structures, and/or, may be linked to the silica dioxide skeleton via the terminal groups' covalently.   *E. coli* ATCC 10536, *S. enterica subsp. enterica serov typhymurium* CECT 722 and *L. monocytogenes* CECT 935 were used to determine the antibacterial activity of the samples.
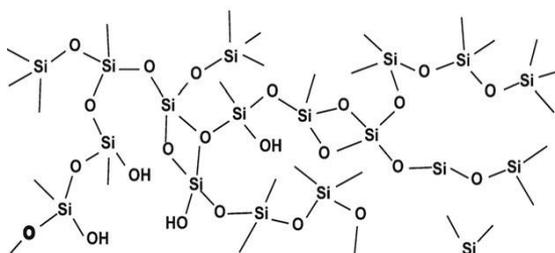

Fig (5). The silicon dioxide skeleton for aerogel and cryogel samples

The total number of bacterial cells that inoculated to the samples (30×30 mm in size) was determined after application of the TEMPO® method. US Department of Agriculture (USDA) have added bioMérieux TEMPO® System to Microbiology Laboratory Guidebook, the Standard-Setting Guideline for Food-Safety Testing in the U.S. [**102**].   So, the % reduction of each bacterial type was determined by using bioMerieux TEMPO® system, based on the methodology of the ISO standard :**ISO 22196:2007 [103]**. The number of bacterial cells, which was recovered from the test textile, is compared to the number of bacteria initially present after incubation with an untreated (+ve) and pure (-ve) control pieces.

The samples were inoculated with 5.25E+05 UFC for *E. coli*, 2.75E+05 for *S. typhimurium*, and 2.75E+05for *L. monocytogenes*. As shown in **Table (4)**, samples treated with 500ng and 1mg of the antibacterials compounds mixture and the positive control inhibited completely the bacterial growth as confirmed by the decreased number of logs for the bacterial growth. While for the negative control, the numbers of bacterial cells increased; indicating that

International Journal of Advance Research in Science and Engineering
Volume No.06, Issue No. 11, November 2017
www.ijarse.com

IJARSE
ISSN: 2319-8354

the pure samples (-ve control) did not show any antibacterial activity. The reduction observed with *Listeria sp.* may be attributed to an artifact.

Table 4. Antibacterial activity of cryogel silica film loaded with a mixture of antibacterial compounds.

Bacterial strain	UFC inoculated/sample	Antibacterial concentration			
		500 ng	1 mg	+ve control	-ve control
Escherichia coli ATCC 10536	5.25E+05	0.00E+00	0.00E+00	0.00E+00	9.20E+06
Salmonella enterica subsp. enterica serov typhymurium CECT 722	2.75E+05	0.00E+00	0.00E+00	0.00E+00	9.60E+05
Listeria monocytogenes CECT 935	2.75E+05	0.00E+00	0.00E+00	0.00E+00	6.57E+04

Interestingly, while the antibacterial activity of the used compounds mixture has been previously confirmed, the antibacterial activity of the positive control cryogel silica film has not been observed before to our knowledge.

More evaluation tests for the cryogel silica film include testing of additional microbial species, and evaluations of the film shelf life are under investigation. Also solving the problems which facing the immobilization of antimicrobials in the aerogel film are under investigation. Finally we can say that, although the impossibility of forming free silica film that can be used as food packing film; we overcame this problem by adsorbing the silica on natural cellulosic materials which act as a holder to the film and use its unique characteristics as a food packaging film afterwards.

IV. CONCLUSION

Aerogels and cryogels show great promise for using in variety of technological areas where special physico-chemical properties are required. As far as we are aware, we have explored new different silica gel synthesis procedure to produce aerogel and cryogel silica films with similar properties to those prepared previously; particularly in terms of porosity and surface area. For the free solid films, they showed high specific surface areas;881 m²/g for the aerogel, and 723 m²/g for the cryogel. The coating and dispersion of SiO_2 of cotton gauze and non woven textile has been studied by SEM. The food packaging films that will prepare from cryogel silica immobilize with suitable biologically active antimicrobials; the film will have double effects. The first antimicrobial effect will obtain immediately after the packaging step, through the activity of the immobilized antimicrobial compounds; then the long-term-stored packaged food products will maintain preserved through the activity of the silica film. So we can conclude that, aerogels and cryogels are considered as promising techniques

International Journal of Advance Research in Science and Engineering
Volume No.06, Issue No. 11, November 2017
www.ijarse.com

IJARSE
ISSN: 2319-8354

for several food packaging applications in the future. Although the technical challenges, including the cost, for replacing conventional food packaging materials with those techniques. Therefore, the efficiency of those techniques must be marketed to both the producers and consumers.

V. ACKNOWLEDGMENTS

REFERENCES

[1] S. Burt, Essential oils: their antibacterial properties and potential applications in foods—a review, *International journal of Food Microbiology, 94(3), 2004, 223–253.*

[2] P. Suppakul, Moisture sorption characteristics of cassava flour film, Proc. 15th world conference on packaging, *International Association of Packaging Research Institutes (IAPRI), Tokyo, 2006, 113-117.*

[3] N.De Kruijf, M. van Beest, R. Rijk, T. Sipilainen-Malm, P.P. Losada, and B. De Meulenaer, Active and intelligent packaging: applications and regulatory aspects, *Food Additives and Contaminants journal, 19(4), 2002, 144–162.*

[4] I. Sánchez-Ortega, B. E. García-Almendárez, E.M. Santos-López, A. Amaro-Reyes, J. E. Barboza-Corona, and C. Regalado, Antimicrobial edible films and coatings for meat and meat products preservation–review, *The Scientific World Journal, 2014, Article ID 248935, 2014, 18 pages.*

[5] S. W. Ruban, Biobased Packaging - Application in meat industry–review, *Journal of Veterinary World, 2(2), 2009.*

[6] T. Bourtoom, Edible films and coatings: characteristics and properties –review, *International Food Research Journal, 15(3), 2008, 237-248.*

[7] Y.D. Chi-Zhang, K.L. Yam, and M.L. Chikindas, Effective control of *Listeria monocytogenes* by combination of nisin formulated and slowly released into a broth system, *International journal of Food Microbiology, 90(1), 2004, 15–22.*

[8]) Y.M. Kim, D.S. An, H.J. Park, J.M. Park, and D.S. Lee, Properties of nisin-incorporated polymer coatings as antimicrobial packaging materials, *Packaging Technology and Science, 15(5), 2002, 247–254.*

[9] B. Ouattara, R.E. Simard, G. Piette, A. Begin, and R.A. Holley, Diffusion of acetic and propionic acids from chitosan-based antimicrobial packaging films, *Journal of Food Science, 65(5), 2000, 768–773.*

[10] V. Coma, Bioactive packaging technologies for extended shelf life of meat–based products, *Journal of Meat Science, 78, 2008, 90–103.*

[11] D. Dainelli, N. Gontard, D. Spyropoulos, E. Zondervan-van den Beuken, andP. Tobback, Active and intelligent food packaging: legal aspects and safety concerns- review, *Trends in Food Science and Technology, 19, 2008, 103-104.*

[12] G.L. Robertson, Food Packaging Principles and Practice, 2nd edn.*Boca Raton, Florida: CRC Press, 2006.*

[13] M. Rojhan, and L. Nouri, Antimicrobial, physicochemical, mechanical, and barrier properties of *Tapioca* Starch films incorporated with *Eucalyptus* Extract, *Journal of Chemical Health Risks, 3, 2013, 43-52.*

[14] T. Mehdizadeh, H. Tajik, S.M.R. Rohani, and A.R. Oromiehie, Antibacterial, antioxidant and optical properties of edible starch - chitosan composite film containing *Thymus kotschyanus* essential oil, *Journal of Veterinary Research Forum, 3, 2012, 167-173.*

[(15] J. A. Pennington, Silicon in foods and diets, *Journal of Food Additives and Contaminants; 8(1), 1991, 97-118.*

[16] *S.Dekkers*, P. Krystek, R.J.B. Peters, and D.P.K.Lankveld, Presence and risks of nano-silica in food products, *Journal of Nanotoxicology, 5(3), 2011, 393-405.*

[(17] Food and Drug Administration (FDA), GRAS notification for synthetic amorphous silica, U.S. food and drug administration, office of food additive safety (HFS-200), center for food safety and applied nutrition, *5100 Paint Branch Parkway, College Park, MD 20740-3835; 2014, 1-16.*

[18] *International Agency for Research on Cancer* (IARC*)*, Silica, some silicates, coal dust and para-aramid fibrils, *IARC monographs on the evaluation of carcinogenic risks to humans, 68, 1997, 41-242.*

[19] Food and Drug Administration, Notification of the GRAS determination of silicon dioxide when added directly or indirectly to human food, Eliot Harrison, Lewis and Harrison, Agent for Cabot. Office of food additive safety, center for food additive safety and applied nutrition, *5 100 Paint Branch Parkway, College Park, MD 20740, 2010.*

[20] Food and Agriculture Organization and World Health Organization (FAO/WHO), Silicon dioxide amorphous, calcium, magnesium, and sodium alumina silicates, Thirteenth report, of the Joint FAO/WHO expert committee on food additives, *FAO nutrition meetings report series, world health organization technical report series, 1969.*

[21] EU Regulation, Scientific opinion of the panel on food additives and nutrient sources added to food on calcium silicate, silicon dioxide and silicic acid (gel added for nutritional purposes to food supplements) - following a request from the European Commission, *The EFSA Journal, Regulation (EU) 2009, 1132, 1-24,* available at: http://www.efsa.europa.eu/en/scdocs/doo/ans ei 1132

[22] A. Pons, LI. Casas, E. Estop, E. Molins, K.D.M. Harris, and M. Xu, A new route to aerogels: monolithic silica cryogels, *Journal of Non-crystalline Solids, 358, 2012, 461–469.*

[23] W. Yin, S. M. Venkitachalam, E. Jarrett, S. Staggs, N. Leventis, H. Lu, and D. A. Rubenstein, Biocompatibility of surfactant-templatedpolyurea-nano encapsulated macroporous silica aerogels with plasma platelets and endothelial cells, *Journal* of *Biomedical* Materials Research; part A, 92, 2010, 1431–1439.

[24] S. Gao, Y. Wang, T. Wang, G. Luo, and Y. Dai, Immobilization of lipase on methyl-modified silica aerogels by physical adsorption, *Bioresource Technology* journal*, 100, 2009, 996–999.*

[25] S. Gorle, I. Smirnova, and M. McHugh, Adsorption and thermal release of highly volatile compounds in silica aerogels, *Journal of Supercritical Fluids*; 48, 2009, 85–92.

[26] C. S. Kicinski, Preparation and characterization of energetic nano composites of organic gel – inorganic oxidizers, *Propellants, Explosives, and Pyrotechnics journal, 34, 2009, 155.*

[27] O. A. Shlyakhtin, and Y. J. Oh, Inorganic cryogels for energy saving and conversion, *Journal ofElectroceram, 461(23), 2009, 452.*

[28] C.C. Egger, C. du Fresne, D. Schmidt, J. Yang, and V. Schadler, Design of highly porous melamine-based networks through a bicontinuous microemulsion templating strategy, *Journal of Sol-Gel Science and Technology, 48, 2008, 86–94.*

[29] Y. K. Li, M. J. Chou, T. Y. Wu, T. R. Jinn, and Y. W. Chen-Yang, A novel method for preparing a protein encapsulated bioaerogel: using a red fluorescent protein as model, *Acta Biomaterialia journal, 4, 2008, 725–732.*

[30] J. K. Lee, and G. L. Gould, Polycyclopentadiene based aerogel: a new insulation material, *Journal of Sol-Gel Science and Technology, 44, 2007, 29–40*

[31] G. Carlson, D. Lewis, K. McKinley, J. Richardson, and T. Tillotson, Aerogel commercialization: technology, markets and costs, *Journal of Non-crystalline Solids, 186, 1995, 372-379.*

[32] S. S. Prakash, C. J. Brinker, A. J. Hurd, and S. M. Rao, Silica aerogel films prepared at ambient-pressure by using surface derivatization to induce reversible drying shrinkage, *Journal of Nature, 374, 1995, 439-443.*

[33] L. Zuo, Y. Zhang, L. Zhang, Y. Miao, W. Fan, and T. Liu, Polymer/carbon-based hybrid aerogels: preparation, properties and applications-review, *Materials, 8, 2015, 6806–6848.*

[34] D.E. Mihaiescu, R. Cristescu, G. Dorcioman, C.E. Popescu, C. Nita, G. Socol, I .Mihailescu, A. M. Grumezescu, D. Tamas, M. Enculescu, R.F. Negrea, C. Ghica, C. Chifiriuc, C. Bleotu, and D.B. Chrisey, Functionalized magnetite silica thin films fabricated by MAPLE with antibiofilm properties, *Journal of Biofabrication, 5, 2013, 1-10.*

[35] C. A. Garcia-Gonzalez, M. C. Camino-Rey, M. Alnaief, C. Zetzl, and I. Smirnova, Supercritical drying of aerogels using CO_2: Effect of extraction time on the end material textural properties, *Journal of Supercritical fluids, 66, 2012, 297-306.*

[36] A. Kimberly, D. Obrey, V. Kennard, W. Douglas, and A. Loy, Enhancing mechanical properties of silica aerogels, *Journal of non-crystalline Solids, 357, 2011, 3435.*

[37] C. Mu, F. Liu, Q. Cheng, H. Li, B. Wu, G. Zhang, and W. Lin, Collagen cryogel cross-linked by dialdehyde starch, *Macromolecular Materials and Engineering journal, 295, 2010, 100-107.*

[38] B. E. Yoldas, M. J. Annen, and J. Bostaph, Chemical engineering of aerogel morphology formed under non-supercritical conditions for thermal insulation, *Journal of Chemistry* of *Materials, 12(8), 2000, 2475 - 2484.*

[39] B. Zhou, J. Wang, L. Zhao, J. Shen, Z. S. Deng, and Y.F. Li, Preparation of C-60-doped silica aerogels and the study of photoluminescence properties, *Journal of vacuum science and technology B, 18(4), 2000, 2001-2004.*

[40] L. Forest, V. Gibiat, and T. Woignier, Blots theory of acoustic propagation in porous-media applied to aerogels and alcogels, *Journal of Non-crystalline Solids; 225(1), 1998, 287-292.*

[41] Z. Novak, M. Habulin, V. Krmelj, and Z. Knez, Silica aerogels as supports for lipase catalyzed esterifications at sub- and supercritical conditions, *Journal of supercritical fluids, 27(2), 2003, 169-178.*

[42] L. W. Hrubesh, Aerogels: the world's lightest solids, *Journal of Chemical Industries, 24, 1990, 824–827.*

[43] G.C. Bond, and S. Flamerz, Structure and reactivity of titania-supported oxides, Part 3: reaction of isopropanol over vanadia-titania catalysts, *Journal ofApplied Catalysis,33(1),1987, 219-230*

[44] C.A.M. Mulder, and J.G. Van Lierop, Preparation, densification and characterization of autoclave dried SiO_2 gels, In: Aerogels, Fricke, J.(ed.), *Springer, Part of the Springer Proceedings in Physics book series (SPPHY), 6, 1986.*

[45] S. S. Kistler, Coherent expanded aerogels, *Journal of Physical Chemistry, 36, 1932, 52–64.*

[46] D. Robert, S. Barelli, D. Crettaz, P-A. Bart, J. A. Schifferli, D. Betticher, and J-D.Tissot, Clinical proteomics: study of a cryogel, *Journal of Proteomics, 6(13), 2006, 3958–3960.*

[47] H. Schubothe, *Serologie und klinische bedeutung der autohamantikorper, Schweiz. Med. Wochenschrift, 88, 1958.*

[48] I. Smirnova, S. Suttiruengwong, and W. Arlt, Feasibility study of hydrophilic and hydrophobic silica aerogels as drug delivery systems, *Journal of Non-Crystalline Solids, 350, 2004, 54–60.*

[49] D.M. Smith, D. Stein, J.M. Anderson, and W. Ackerman, Preparation of low-density xerogels at ambient pressure,Journal of Non-Crystalline Solids*, 186, 1995, 104–112.*

[50] P.H. Tewari, A. J. Hunt, and K.D. Lofftus, Ambient temperature supercritical drying of transparent silica aerogels, *Journal ofMaterials Letters, 3, 1985, 363-367.*

[51] S.D. Bhagat, and A.V. Rao., Surface chemical modification of TEOS based silica aerogels synthesized by two step (acid-base) sol-gel process,*Journal of Applied Surface Science,252(12), 2006, 4289–4297.*

[52] A. S. Dorcheh, and M.H.Abbasi, Silica aerogel: synthesis, properties and characterization, *Journal of materials processing technology, volume 199, 2008, 10–26*

[53] E.M. Arndt, M.D. Gawryla, and D.A. Schiraldi, Elastic, low density epoxy/clay aerogel composites, *Journal of Materials Chemistry, 17(33), 2007,3525–3529.*

[54] R. Kocklenberg, B. Mathieu, S. Blacher, R. Pirard, J. P. Pirard,R. Sobry, and G. Vanden Bossche,Texture control of freeze-dried resorcinol-formaldehyde gels, *Journal of Non-crystalline Solids, 225, 1998, 8–13.*

[55] Y. D. Tretyakov, and O. A. Shlyakhtin, Recent progress in cryochemical synthesis of oxide materials, *Journal of material Chemistry,9, 1999, 19–24.*

[56] S.H. Hyun, T.Y. Kim, G.S. Kim, and H.H.Park, Synthesis of low-k porous silica films via freeze drying,*Journal of Materials Science Letters; 19(20), 2000, 1863.*

[57] G. M. Pajonk, M. Repellin-Lacroix, S. Abouarnadasse,; J. Chaouki, and D. Klvana, From sol-gel to aerogels and cryogels, *Journal of Non-crystalline Solids, 121, 1990, 66–67.*

[58] M. Ye, H. Neetoo, and H. Chen, Control of *Listeria monocytogenes* on ham steaks by antimicrobials incorporated into chitosan- coated plastic films, *Journal of Food Microbiology, 25(2),2008, 260–268.*

[59] P. Appendini, and J.H. Hotchkiss, Review of antimicrobial food packaging „*Journal of Innovative Food Science and Emerging Technologies, 3(2), 2002, 113–126.*

[60] S. Quintavalla, and L. Vicini, Antimicrobial food packaging in meat industry, *Journal of Meat Science, 62(3), 2002, 373–380.*

[61] S. Bhattacharyya, A. Agrawal, C. Knabe, and P. Ducheyne, Sol-gel silica controlled release thin films for the inhibition of methicillin-resistant *Staphylococcus aureus*, *Biomaterials journal, 35, 2014, 509-517.*

[62] V. Dhapte, S. Kadam, V. Pokharkar, P. K. Khanna, and V. Dhapte, Versatile SiO_2 nanoparticles at polymer composites with pragmatic properties, *Hindawi Publishing Corporation, ISRN Inorganic Chemistry,2014, 8 pages.*

[63] A. S. Elnawawy, M. S. Khalil, and R. M.Mohareb, Semi-synthesis of nano-antibacterial heterocyclic compounds from the *Streptomyces candidus* secondary metabolites as food additives, *Journal of scientific and engineering research, 4(10), 201, 421-434.*

[64] G.W. Scherer, and D.M. Smith, Cavitation during drying of a gel, *Journal of Non-Crystalline Solids, 189, 1995, 197–211.*

[65] C.J. Brinker, and G.W. Scherer, Sol–gel Science, The physics and chemistry of sol– gel processing, *academic, New York, 1990, 581–585.*

[66] L. Qian, and H. Zhang, Controlled freezing and freeze drying: a versatile route for porous and micro-/nano-structured materials, *Journal of Chemical Technology and Biotechnology, 86(2),2011, 172-184.*

[67] H. Maleki,L. Durães, and A. Portugal, An overview on silica aerogels synthesis and different mechanical reinforcing strategies, *Journal of Non-Crystalline Solids, 385, 2014, 55-74.*

[68] L. Onnby, application of cryogels in water and wastewater treatment (ch.12),In: *supermacroporous cryogels-biomedical and biotechnological applications,* Kumar, A. (ed),*CRC Press, 2016, 335–364.*

[69] H. Yavuz, N. Bereli, G. Baydemir, M. Andaç, D. Türkmen, and A.Denizli, Cryogels: Applications in extracorporeal affinity therapy (Chapter 14), In: *supermacroporous cryogels- biomedical and biotechnological applications,* Kumar, A. (ed), *CRC Press, 2016, 391–420*

[70] T.M. A. Henderson, K. Ladewig, D. N. Haylock, K. M. McLean, and A. J. O'Connor, Cryogels for biomedical applications, *Journal of Materials Chemistry, part B,1(21),2013, 2682-2695.*

[71] S.C. Rodrigues, C. L. Salgado, A. Sahu,M. P. Garci,M. H. Fernandes, and F. J. Monteiro, Preparation and characterization of collagen-nano hydroxyapatite biocomposite scaffolds by cryogelation method for bone tissue engineering applications, *Journal of Biomedical materials research, part A, 101, 2013, 1080-1094.*

[72] T. Mehling, I. Smirnova, U. Guenther, and R. H. H.Neubert, Polysaccharide-based aerogels as drug carriers, *Journal of Non-Crystalline Solids, 355(50–51), 2009, 2472–2479.*

[73] R. Gavillon, and T. Budtova, Aerocellulose: new highly porous cellulose prepared from cellulose-NaOH aqueous solutions, *Biomacromolecules journal, 9, 2008, 269–277.*

[74] D. A. Schiraldi, M. D. Gawryla, J. R. Johnson, and J. Griebel, Functional materials based on clay aerogels, *Polymer Preprints journal, 48, 2007, 988–989.*

[75] I. Smirnova, S. Suttiruengwong, and W. Arlt, Aerogels: tailor-made carriers for immediate and prolonged drug release,*KONA powder and particle journal, 23, 2005, 86.*

[76] I. Smirnova, J. Mamic, and W. Arlt, Adsorption of drugs on silica aerogels, *Langmuir journal, 19(20), 2003, 8521–8525.*

[77] J. M. Wallace, J. K. Rice,J. J. Pietron, R. M. Stroud, J. W. Long, and D. R. Rolison, Silica nano architectures incorporating self-organized protein superstructures with gas-phase bioactivity, *Nano Letters, 3, 2003, 1463–1467.*

[78] K. Sinkó, Influence of chemical conditions on the nanoporous structure of silicate aerogels, Materials *Journal, 3, 2010, 704-740.*

[79] B.Karmakar, G. De, and D.Ganguli, Dense silica microspheres from organic and inorganic acid hydrolysis of TEOS, *Journal of Non-Crystalline Solids,272(2-3), 2000, 119–126.*

[80] F. Kirkbir, H. Murata, D. Meyers, S. Ray Chaudhuri, and A. Sarkkar,Drying and sintering of sol-gel derived large SiO$_2$ monoliths, *Journal of Sol-Gel Science and Technology, 6(203), 1996.*

[81] N. Hüsing, and U. Schubert, Aerogels, Ullmann's Encyclopedia of Industrial Chemistry, Wiley- VCH, Weinheim, 2006.

[82] E. Ponthieu, E. Payen, G. M. Pajonk, and J. Grimblot, Comparison of drying procedures for the preparation of alumina powders with the system Al-alkoxide/ tertiary butanol/water, *Journal of Sol-Gel Science and Technology, 8, 1997, 201–206.*

[83]K. Kamiuto, S. Saitoh, and Y. Tokita, Scattering phase function of a silica aerogel at 450 nm wavelength, *Journal of Quantitative Spectroscopy and Radiative Transfer, 50(3), 1993,293-299.*

[84] R. E. Russo, and A.J. Hunt, Comparison of ethyl versus methyl sol-gels for silica aerogels using polar nephelometry, *Journal of Non-Crystalline Solids,86(1-2), 1986, 219-230.*

[85]A. J. Hunt, and P. Berdahl, structure data from light scattering studies of aerogel, Materials Research Society Symposium – Proc, 32, 1984, 275.

[86] G. Zhang, R.Qu, C. Sun, C. Ji, H. Chen, and C. Wang, Adsorption for metal ions of chitosan coated cotton fiber, *Journal of Applied Polymer Science, 110, 2008, 2321.*

[87]N. Li, and R. B. Bai, Copper adsorption on chitosan-cellulose hydrogel beads: Behaviors and mechanisms, *Separation and Purification Technology journal, 42, 2005, 237–247.*

[88]X. D. Liu, N. Nishi, S. Tokura, and N. Sakairi, Chitosan coated cotton fiber: Preparation and physical properties, *Journal of Carbohydrate Polymers, 44, 2001, 233.*

[89] F. Shi, L. Wang, and J. Liu, synthesis and characterization of silica aerogels by a novel fast ambient pressure drying process, *Materials Letters journal, 60, 2006, 3718.*

[90]G. S. Kim, and S. H.Hyun, Synthesis and characterization of silica aerogel films for inter-metal dielectrics via ambient drying, *Thin Solid Films, 460, 2004, 190–200.*

[91]A.V. Rao, and P.B. Wagh, preparation and characterization of hydrophobic silica aerogels, *Materials ChemistryandPhysics,53, 1998, 13–18.*

[92]K.S.W. Sing, D. H. Everett, R. A.W. Haul, L.Moscou, R. A. Pierotti, J. Rouquerol, and T. Siemieniewska, Reporting physisorption data for gas/solid interface with special reference to the determination of surface area porosity, *Pure Applied Chemistry journal, 57, 1985, 603.*

[93] N. Husing, and U. Schubert, Aerogels- airy materials, *Angewandte Chemie International Edition journal, 37, 1998, 22-55.*

[94]A. Duran, J.M. Fernandez-Navarro, P. Casariego, and A. Joglar, Optical properties of glass coatings containing Fe and Co., *Journal of Non-Crystalline Solids,82(1-3), 1986, 391-399.*

[95]A.Hilongaa, j. Kimb, P. B. Sarawadea, and H. T. Kima, Low-density TEOS-based silica aerogels prepared at ambient pressure using isopropanol as the preparative solvent, *Journal of Alloys and Compounds, 487, 2009, 744–750.*

[96] N.O. Gopal, K.V.Narasimhulu, and J.L. Rao,EPR, optical, infrared and Raman spectral studies of actinolite mineral, *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy, 60 (11), 2004, 2441–2448*

[97]G. Socrates, Infrared and Raman characteristic group frequencies: tables and charts, third ed., Wiley, *245, 2001.*

[98] R. Al-Oweini, and H. El-Rassy, Synthesis and characterization by FTIR spectroscopy of silica aerogels prepared using several Si (OR)$_4$ and R-Si (OR')$_3$ precursor, *Journal of Molecular Structure, 919, 2009, 140–145*

[99] Sh. Al-Kandary, A. A. M. Ali, and Z. Ahmad, Morphology and thermo-mechanical properties of compatibilized polyimide-silica nanocomposites, *Journal of Applied Polymer Science, 98(6), 2005, 2521–2531.*

[100] F. Al-Sagheer, and S.Muslim, Thermal and Mechanical Properties of Chitosan/SiO$_2$ Hybrid Composites, Journal of Nanomaterials, 2010, Article ID 490679, 2010.

[101] Z. Ahmad, F. Al-Sagheer, A. A. M. Ali, and S. Muslim, Interphase bonding in poly (hyroxyamide)-silica hybrids: effect of isocyanto-propyltriethoxysilane addition on the structure and properties, *Journal of Macromolecular Science A; 44(1) 2007, 79–90.*

[102] BioMerieux, USDA adds bioMérieux TEMPO® System to microbiology laboratory guidebook, the standard-setting guideline for food-safety testing in the U.S., 2015,bioMérieux industry website: http://www.biomerieux-industry.com.

[103] ISO 22196, Plastics - measurement of antibacterial activity on plastics surfaces, Published in Switzerland, 2007.