Development of new sol-gel materials with citrus waste based on the principles of the circular economy

ABSTRACT

Circularity is at the core of eco-design, the production methodology in which waste is repurposed and environmental impacts such as raw-material use, are reduced through reuse and recycling. The scale of global waste and its proportionate economic and environmental costs is gargantuan. Faced with this entrenched dynamic, how can closed-loop systems become the norm? One answer is to integrate them into circular economies. This model looks to extend the life of products at the use stage, retaining value.
In this research, the sol-gel method is carried out through acid or alkaline hydrolysis, combined with orange or lemon peels generated as urban waste. The main objective was to obtain silica-based materials with the tetraethylorthosilicate precursor using acidic and basic catalysts, of organic and inorganic origin. The solids obtained were characterized with SEM, FT-IR, potentiometric titration and XRD. The main objective was to use an amount of bio-waste to study the influence on the hydrolysis of the sol-gel method, the influence on the morphology and acidity of the synthesized solids.
According to the results, the bio waste used can provide acidity, although not completely replace it. The acidity values obtained using bio-waste are similar to those of pure silica with acid hydrolysis, showing promising results. Considering that citrus fruits are cultivated and used worldwide, each year significant amounts of waste are produced and derivatives such as cellulose, lignin, pectin, pigments, essential oils, etc. can be used. From which the pharmaceutical, cosmetic, food and even energy sectors have benefited so far.

Keywords: circular economic; sol-gel method; silica-based materials; bio-waste; lemon peels; orange peels;

1. INTRODUCTION

The idea of a circular economy already appears in the book by Pearce and Turner [1] on Economics of Natural Resources and the Environment. In fact, chapter 2 of the book is titled “The circular economy (CE)”. However, who was the creator of the beginnings of this type of economy? Ellen MacArthur understood that the resources she used to feed herself and for her ship to move were what determined that her trajectories were good. Without them, her knowledge would not allow her to reach any port. The Ellen MacArthur Foundation, founded in 2010, defines CE as a move from a linear model of resource consumption to an economy that is restorative [2]. According to the concept of Kane et al. [3] CE is a holistic philosophy used to manage and preserve resources through recovery and reuse (circularity). It outlines ways to eliminate waste, transform biodegradable and non-biodegradable waste, and promote reuse and recycling. There are different forms of circularity (Figure 1), with the 9R model being the optimal application: Refuse, Rethink, Reduce, Reuse, Repair, Restore, Remanufacture, Reuse, and Recycle and Recover [4-6].

Fig. 1. Circular Economic diagram

The EC has grown rapidly to achieve the United Nations Sustainable Development Goals (SDGs) and a key objective of the EC is to create successful sustainability [7]. With the amount of agricultural waste that is generated, the processes for the development by EC of new materials from

citrus waste is a task of high economic and social cost [8]. The waste is not processed with techniques appropriate to each type of waste and its end is generally an open landfill. Research groups [9-17] work on citrus since it is an economical renewable resource for the production of bioactive molecules in different industries. In Argentina, a ton of garbage is generated every 2 seconds according to the Ministry of Environment and Sustainable Development: Circular economy: everything together is garbage but separately it is resources [18]. With the growing importance that organic farming has acquired, both in developed and developing countries, geographically there are no studies of these socio-economic realities [19]. Organic agriculture [20, 21] has remained a haven against the invasion of agro-chemicals and industrialization in the food supply chain. It represents less than 1% of global agriculture, specifically reported as 0.98% by the study of Willer and Lernoud [22]. On the contrary, agriculture is the fastest growing food sector in the world [23]. South America has a strong presence: Argentina (3,191,255 ha), Uruguay (930,965 ha) and Brazil (705,233 ha) [22-24]. Approximately more than 40% of the oranges produced globally are used in the production of different commercial products [25]. Due to processing, large amounts of bio waste, such as peels in the juice industry, are generated and accumulated [26]. In this research, two main issues were addressed at the same time: the use of citric bio-waste and the obtention of materials using the sol-gel technique, looking for its use in heterogeneous catalysis as a bi-functional support. Silica has been identified as an ideal support for its strong hydrophilicity, acknowledged biocompatibility, shape and chemistry surface [27]. Two different strategies have been explored to combine bio-waste with the synthesis of silica-based materials. The first step is to obtain silica through acidic or alkaline hydrolysis by using acetic and hydrochloric acids (organic and inorganic acids) and an alkali (ammonium hydroxide) for this purpose. In a second step, lemon or orange peels were added to the obtained mixtures. The objective of this mixed synthesis was to find the influence of organic bio-waste on acids/alkali, looking to replace these partially with organic orange or lemon peels, which could presumable, provide acidity. For this, an amount of bio-waste was used in the different syntheses [28, 29].

As a precursor of silica, tetraethyl orthosilicate (TEOS) was used and its hydrolysis and condensation were studied, using absolute ethanol as a green solvent due to its re-newability [30, 31]. This solvent plays an important role in the synthesis, both in the case of the reaction with TEOS, once they act as a homogenizer agent for substances with different solubility's that participate in the condensation reaction, and with lemon and orange peels, extracting compounds of interest from them [32-34]. All synthesized solids were in-depth characterized integrating different physical-chemical techniques, such as Scanning Electron Microscopy (SEM) and Ray-X Difraction (XRD). The chemical composition of solids was investigated through Fourier Transform Infrared Spectroscopy (FT-IR) and acidic properties by *n*-butylamine potentiometric titration. With the physicochemical properties discussed in this research, silica-based materials synthesized with bio waste could have the potential to be used in

different technological processes, as supports for heterogeneous reactions, additives for paints, among others.

2. EXPERIMENTAL DETAILS/METHODOLOGY

The starting point to specifying the proposed objectives includes having the necessary material and carrying out an adequate design of the experiments. For the design of these steps, two levels of complexity are selected, when required. This means that some of the operating variables will remain fixed. Thus, reliable results can be obtained with the fewest possible experiences [35,37]. Before starting with the sol-gel synthesis, the oranges and lemons were peeled (20 of each of them) and the peels obtained were cut off into small pieces. Then put on the stove for 3 days, at 70 °C (Figure 2).

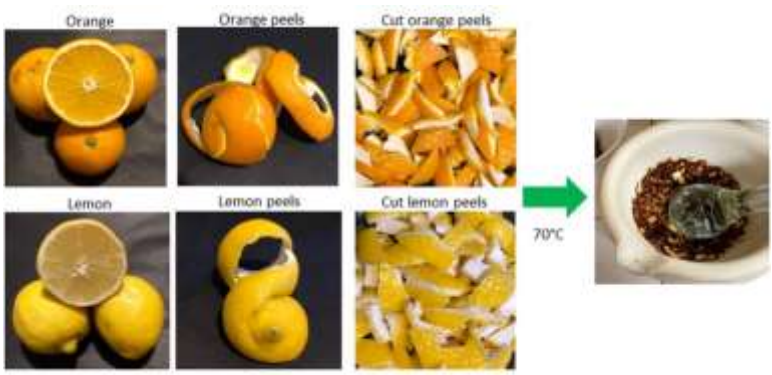

Fig. 2. Treatment of lemon and orange peels.

The sol-gel synthesis was carried out in a chamber with a nitrogen-controlled atmosphere, at room temperature. First, a portion of the solvent, absolute ethanol (CH_3CH_2OH, Carlo Erba), and the corresponding catalyst for acid hydrolysis were placed into a beaker: acetic acid glacial (CH_3COOH, HPLC grade, J.T.Baker), or hydrochloric acid (HCl, 37%, Merck). The same was done in alkaline hydrolysis using ammonium hydroxide (NH_4OH, Anedra analytical reagent). Then, the TEOS ($Si(OC_2H_5)_4$, Aldrich 98%) was added followed by the last portion of solvent and distilled water, respectively. Each mixture, outside the nitrogen controlled atmosphere, was placed on a magnetic stirrer at 500 rpm; the respective amounts of orange or lemon peels were added, maintaining stirring for 2 h. The details of each synthesis are shown in Table 1 to Table 3 (considering the total volume of ethanol added). The amounts of all the reagents were varied in order to maintain the relationship between the TEOS precursor, the acid and alkaline catalysts, and the solvent, with which the same silica-based solids should be generated, but adding citrus peels

Table 1. Conditions employed in silica synthesis using acetic acid as a catalyst.

Sample	Precursor	Solvent	Acid	Water	Bio-waste
SA1	TEOS 17,0 mL	EtOH 21,8 mL	CH_3COOH 5.0 mL	H2O 5,0 mL	Pure silica 5.0 g
SA2	TEOS 8.5 ml	EtOH 10.9 mL	CH_3COOH 2.5 mL	H_2O 2.5 mL	50% orange peel 2.5 g
SA3	TEOS 8.5 ml	EtOH 10.9 mL	CH_3COOH 2.5 mL	H_2O 2.5 mL	50% lemon peel 2.5 g

Table 2. Conditions employed in silica synthesis using HCL as a catalyst.

Sample	Precursor	Solvent	Acid	Water	Bio-waste
SH1	TEOS 17.0 mL	EtOH 21.8 mL	HCl 7.5 mL	H2O 5.0 mL	Pure silica 5.0 g
SH2	TEOS 8.5 ml	EtOH 10.9 mL	HCl 3.8 mL	H_2O 2.5 mL	50% orange peel 2.5 g
SH3	TEOS 8.5 ml	EtOH 10.9 mL	HCl 3.8 mL	H_2O 2.5 mL	50% lemon peel 2.5 g

Table 3. Conditions employed in silica synthesis using NH_4OH as a catalyst.

Sample	Precursor	Solvent	Alkali	Water	Bio-waste
SB1	TEOS 17.0 mL	EtOH 21.8 mL	NH_4OH 11.8 mL	H2O 5.0 mL	Pure silica 5.0 g
SB2	TEOS 8.5 ml	EtOH 10.9 mL	NH_4OH 5.9 mL	H_2O 2.5 mL	50% orange peel 2.5 g
SB3	TEOS 8.5 ml	EtOH 10.9 mL	NH_4OH 5.9 mL	H_2O 2.5 mL	50% lemon peel 2.5 g

The evaluation of the acidic properties was carried out by potentiometric titration with *n*-butylamine using a Metrohm 794 Basic Titrino titrator (Switzerland) with a double-junction electrode. For that, 0.025 mL/min of an *n*-butylamine solution in acetonitrile (0.025 N) was added to 0.025 g of sample, previously suspended in 45 mL of acetonitrile and keeping the stirring time constant (540 s) before to add the first drop, and a waiting time of the drop of 60 s, while stirring constantly. FT-IR spectrum was obtained using Bruker IFS 66 equipment (Germany). Pellets of the sample in KBr, at room temperature, were measured in a range between 500 and 4000 cm^{-1}. SEM was applied to obtain different micrographs of the solids using the JEOL equipment, JSM-6390LV (Japan), with a voltage of 20 kV. Samples were supported on graphite and metallized with a sputtered gold film. Finally, XRD patterns were recorded by means of a PANalyical X'Pert Pro 3373/00 device with the following conditions: Cu Kα radiation (λ=1.5417 Á); Ni filter; 20 mA and 40 kV in the high voltage source; scanning angle (2θ) from 5º to 40º, scanning rate 2º (2θ)/min.

3. Results and Discussion

3.1. Digital Photographs

Among the basic principles of the sol-gel technique [38] is an alternative for obtaining non-metallic inorganic materials, such as glass and ceramics. These are produced at high temperatures. The sol-gel technique [39] consists of hydrolysis and condensation, coming from alkoxide precursors (organometallic compounds) to form a polymer network in a glassy state that typically exhibits a macro or monoporous structure.

The gel is formed through a two-step reaction: a) hydrolysis and b) polycondensation. Stage a) is the hydrolysis for the formation of the gel, which is carried out using different alcohols as solvents. This reaction is produced by the nucleophilic attack of the oxygen present in water on the metal atom, forming silanol groups [40]. The solvent is the chemical compound that represents the largest proportion of the process. The second stage b) is the condensation that begins as soon as the alkoxide groups are hydrolyzed. The concentrations of -OH and/or -OR terminal groups depend on the hydrolysis and condensation mechanisms. Driven by environmental legislations, the establishment of green solvents for extractions, separations, formulations and chemical reactions has become an increasingly important area of research. In this technique, they are determined by the nature of the acid or basic hydrolysis, that is, which catalyst is used [41]. Keeping in mind what was said above, Brinker and Scherer [32] studied the effect of pH on the morphology of siliceous structures. They discovered that the change in the pH of the solution affects the hydrolysis and condensation processes, respectively. Figure 3 shows silica synthesized with acid hydrolysis using acetic acid. The first photograph (pure silica, left) shows the silica obtained without biowaste, with its glassy structure, from a gel that was slowly dried at room temperature.

Fig. 3. Pure silica gel obtained with CH_3COOH (left); 50% orange peel (medium); 50% lemon peel (right).

Milea et al. [42] found that the sol-gel technique gives a new composition to the glass, with superior properties, which come from the synthesis of the gel [35, 37]. Figure 3 shows the silica materials with orange and lemon peel aggregates (middle and right). It is important to note that in both cases the added shells remain in the siliceous structure, mainly on the surface of the dried gel due to condensation: this occurs as the gel dries. If the solids are compared with 50% orange and lemon peel (Figure 3), they become

yellowish and have a surface structure similar to pure silica. This layer of siliceous material is brighter and, it can be said, that this material has a glassy consistency. For a better explanation, the silica-based solid obtained forms two phases for 50% of lemon or orange peel: one given by the compounds extracted by the solvents (ethanol and water) from the peels, varying the pH and, the another phase, by the acid used in the synthesis. Gelation is physically manifested by a drastic increase in the viscosity of the solution [43]. These viscosity changes occur without causing the generation of chemical transformations or endothermic or exothermic changes [44]. The wet gel can be strengthened by aging and by the Ostwald maturation syneresis mechanism [45]. Syneresis is characterized by the contraction of the gel network, produced by the expulsion or extraction of liquid. Smaller particles have a higher solubility, which leads to their precipitation and the formation of larger ones [42]. During drying, the effect of citrus peels on the surface of the synthesized solids indicates that the silicon skeleton becomes increasingly rigid. This implies that the surface tension cannot deform the network, the gel body becomes rigid and at this point the probability of rupture is higher [37, 46].

3.2. Potentiometric Titration Characterization

The acid properties of all the synthesized solids were studied through potentiometric titration with *n*-butylamine which allows knowing the number of acid sites and their acid strength. It is important to clarify that this technique only indicates the mass acidity trend of the solids obtained [47]. To interpret the results obtained, the initial electrode potential (Ei) indicates the maximum acid strength of the surface sites, and the values meq/g solid, in which the plateau is reached, indicate the total number of acid sites. The acid strength of the surface sites can be classified according to the following ranges:

very strong sites Ei > 100 mV
strong sites 0 < Ei < 100 mV
weak sites -100 < Ei < 0 mV
very weak sites Ei < -100 mV

The initial electrode potentials are shown in Table 4. Comparing the Ei of the synthesis with acid hydrolysis samples that use acetic and hydrochloric acid, the presence of free electrons in the acid give a higher acidity. Comparing the use of 50% orange peels in acid hydrolysis versus pure silica (with acetic acid), SA1 gives an Ei of 130 mV for pure silica versus 110 mV for 50% (SA2) (Table 4). Hydrochloric acid has a similar behavior of acetic acid when silica-based solid synthesized with orange and lemon peels are analyzed but an Ei higher. For basic hydrolysis, the use of NH_4OH generates the lowest value in both cases of the bio-waste. When lemon is used, in the samples synthesized with hydrochloric acid, there are a high number of acid sites. Tendency that is not manifested when using acetic acid.

Table 4. Initial electrode potential values of synthesized samples.

Sample	Ei (mV)
SA1	130
SA2	110
SA3	90
SH1	650
SH2	590
SH3	590
SB1	110
SB2	112
SB3	120

At this point, it can be seen that none of the biowaste contributes new strong acid sites to the final material, because the acidity of pure silica decreases with the incorporation of orange or lemon peels in the synthesis. On the other hand, when using ammonium hydroxide the acid sites are neutralized (SB1=110 mV). When the amount of bio-waste is 50%, the acidity of the obtained silica increases slightly compared to pure silica, Ei of SB2 (112 mV) and SB3 (120 mV), respectively.

3.3. SEM Characterization

The pH of the catalyst used for acid hydrolysis determines the texture of the solid and this can be seen in Figure 4. The morphology of SA1 and SH1 is laminar and typical of sol-gel silica. Curran and Stiegman [49] studied the morphology of siliceous structures at very high acid concentrations. Below the isoelectric point, dried xerogels become mesoporous: This is due to the protonation of silanols (-SiOH) to produce (-SiOH2+), which are leaving groups and, increase the condensation rate. First, hydrated monomers obtained from the hydrolysis of precursors undergo condensation reactions, forming silicate polymer chains and then small nuclei. These grow through bonds of the silica monomer and the polymer, forming primary particles, with an average diameter of 5 to 7 nm in diameter [50]. In the case of alkaline hydrolysis, sample SB1 gives rise to groups of spheres, as it is a slower hydrolysis (formation of branched polymers or spherical aggregates). This was expected, since the use of a single alkoxide combined with chosen amounts of reagents allows deep control over the nucleation and growth processes, leading to spherical and highly monodisperse nanoparticles [51].

Regarding the SEM micrographs (Figure 5), the samples prepared with HCl as catalyst are presented. It is possible to observe a similarity with the characteristic lamellar format of silica regardless of orange or lemon added to the synthesis. In this case, hydrolysis with this strong acid can form, on the one hand, only silica and, on the other, leach the shells, as can be seen in the micrographs.

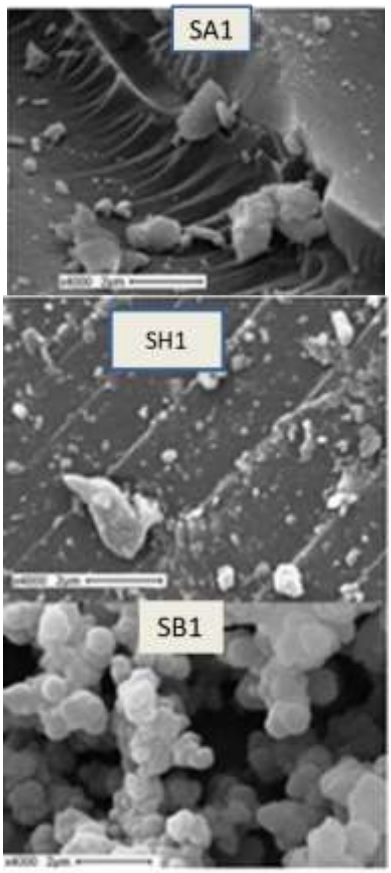

Fig. 4. SEM micrographs of synthesized silica-based solid by acid (SA1 and SH1) and alkali (SB1) hydrolysis. Magnification x4000 (Bar: 2µm).

According to Zarib and Abdullah [52], they obtained a smooth and rough surface for a silicate particle; In this case, rice husk was used as bio-waste. The NH_4OH sample has a rounded shape and its particles form clusters of variable size, similar to SB1 shown in Figure 4. This may be due to the action of the orange and lemon aggregates that modify the pH of the synthesis. An agglomeration of nanoparticles of silica-based material and bio-waste is observed, due to three-dimensional hydrophilic networks on the surface of the solids [53]. Other researchers have synthesized silica with low surface microspheres from wheat husk ash with an alkaline and acid precipitation process [54].

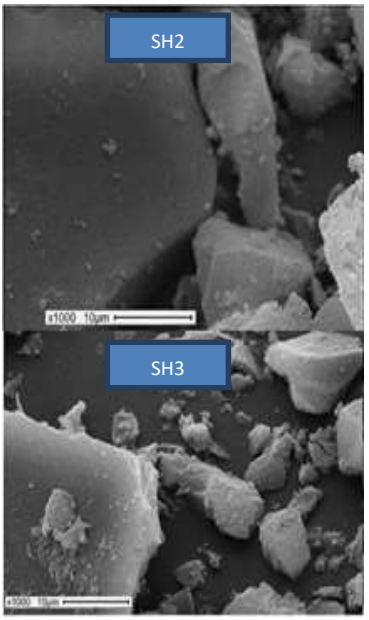

Fig. 5. SEM micrographs of the silica-based solid synthesized using HCl with orange and lemon peels.
Magnification x1000 (Bar: 10µm).

3.4. XRD Characterization

The structure of the synthesized materials was determined using the XRD technique. This conventional technique has been increasingly used in similar studies for mixed matrices using bio-waste, such as the work developed by Worathanakul et al. [55] in which bagasse ash is used as silica source for zeolite synthesis, another alternative source for production of valuable materials and chemicals. The X-ray diffraction diagrams of all silica samples present an amorphous structure of silica xerogels which was confirmed by the broad peaks in the range around 15-30° 2θ, as reported by Czarnobaj [56]. Furthermore, due to the band located around 23° 2θ, which is the typical diffraction of this type of silica [57, 58].

3.5. FT-IR Characterization

FT-IR spectroscopy has been widely used for the characterization of materials synthesized by the sol-gel method [55, 59]. This allowed for indepth analysis to understand the relationships between the material properties, including its structure at the atomic level, and the IR spectrum. As the structure evolves in the silica xerogel, a three-dimensional network of

interconnected tetrahedral unit's forms. FT-IR allows, depending on the width and position of the bands, to characterize the material by interpreting its composition and structure. In this study the region of 4000-500 cm^{-1} was used.

Table 5 shows the characteristic absorption bands of silica obtained with acetic acid as catalyst (SA1). Figure 6 shows the complete FT-IR spectra of the samples synthesized with TEOS as precursor and as acid catalysts: acetic acid (SA1) and hydrochloric acid (SH1). In addition, it is complemented with ammonium hydroxide (SB1) as an alkaline catalyst. Figure 6 and Table 5 show bands that vary at 500, 800, 950, 1080 and 1200 cm^{-1}, which are characteristic bands of silica, corresponding to vibrations of the silicon-oxygen bonds. These bands can be classified by the movement (rolling, bending and stretching), of the oxygen atom related to the silicon atoms [60]. The symmetric and asymmetric stretching modes of Si-O-Si bonds can be assigned to bands of 1166 and 1079 cm^{-1}, respectively. The vibration at 797 cm^{-1} is associated with symmetric stretching of the Si-O bond or vibration modes of ring structures. The bands centered at 948 and 1864 cm-1 are assigned to the vibration of Si-O bonds (silanols) and are characteristic of silica xerogel [61]. The band located around 566 cm^{-1} is attributed to the deformation of cyclotetrasiloxanes (four-membered siloxane rings). This molecule may constitute a large fraction of the oligomeric species present in TEOS-derived systems because they are stable during hydrolysis processes [62].

Table 5. FT-IR of silica synthesized with acetic acid (SH1).

Wavenumber (cm^{-1})	Band assignment	Functional group
3778	Si-OH	Si-OH
3443	v OH [1]	O-H bonded
2926	va (CH_2) [2]	0
1883	vβ Si-O [3]	Si-OH
1640	δ H-O-H [4]	H-O-H
1182	vS (Si-O-Si) [5]	Si-O-Si
1079	va (Si-O-Si) [2]	Si-O-Si
945	vβ (Si-O) [3]	Si-OH
797	vs (Si-O) [6]	Si-O-Si
555	v (Si-O) [1]	SiO_2

[1] v: vibration stretching; [2] va: anti-symmetrical vibration stretching; [3] vβ: symmetric vibration stretching; [4] δ: deformation vibration; [5] vS: symmetric deformation vibration; [6] vs: symmetrical.

The broad band located between 3000 and 3700 cm^{-1} is assigned to the OH species due to the stretching vibrations of hydrogen-bonded water molecules on the silica surface [63], molecular water-bound silanols, silanols free on the surface of the gel [64, 65]. The band located at 1639 cm^{-1} is assigned to the deformation of molecular water and results from the angular deformations of the H-O-H bonds in H_2O. The description made for the SA1 silica sample is common for the other two pure silicas (SH1 and SB1, respectively). Continuing with the FT-IR study of the synthesized samples, the band that appears at 2932 cm^{-1} can be assigned to the symmetric and asymmetric stretching of the C-H bonds in the residual groups CH_3-OH and CH_3-O-Si [64]. Two absorption bands are observed at 1409 and 1518 cm^{-1} due to the CH_3 groups contributed by the organic material (bio-waste). These bands are characteristic of a hydrophobic silica.

All the characterizations used and discussed represent the first part of an extensive study in which we highlight the initial stage of understanding the morphology and behavior of mixed silica supports. These solids were synthesized using a certain amount of biowaste (lemon or orange peel) and acid and basic catalysts, to analyze the influence that said biowaste has on the sol-gel reaction of the solid based on an alkoxide. Based on this knowledge and, in previous studies on the same topic [28, 29], orange and lemon biowaste can provide acidity for the reaction with the TEOS precursor. The results obtained indicate that it could be possible to partially replace the acid catalysts used in this synthesis with bio-waste. Since these subtly reduce the acidity of the mixed materials compared to pure silica. This is because the acidity of the acids used is greater than the amount of acidic compounds that are extracted from the citrus peels used to obtain the mixed matrices

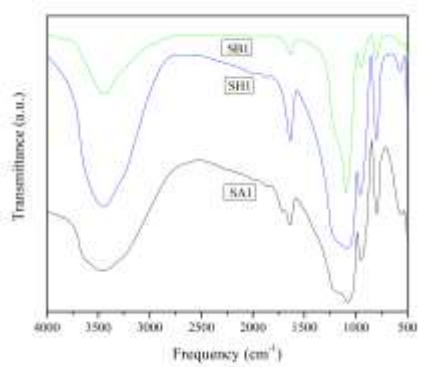

Fig. 6. FT-IR spectrum of the pure silica obtained by synthesis with TEOS as a precursor and acetic acid (SA1, hydrochloric acid (SH1) and ammonium hydroxide (SB1).

4. CONCLUSION

In this study, we synthesized new materials using the sol-gel method, a simple and fast technique that allowed the inclusion of bio-waste in silica matrices, proposing a first stage for the development of a new silica-based support that can be used in heterogeneous catalysis. The analyses of the influence of the orange and lemon peels percentage in the in the acidity and in the morphology of siliceous solids revealed promising results, suggesting that , the bio-waste used can provide acidity to partially replace the acid catalysts investigated in acid hydrolysis, but it is not possible to replace them completely. In addition, the mixed materials also showed the ability to maintain the siliceous structure. Waste (increase in entropy) is an inevitable byproduct of any work done on materials used within the economy (from extraction, through manufacturing, to use and eventual recycling), leading to a decrease in the quantity and/or quality of those materials [65]. For a model that fits so perfectly into ecological thinking, the circular economy is a surprisingly respectable concept. In 1966, the economist Kenneth Boulding [66] addresses the concept of entropy, giving a description of the thermodynamics of the circular economy, highlighting the importance of both energy and information. In other words, the conditions of the physical system for the circular economy now have philosophical, ethical and economic dimensions. This author is surprisingly prescient, enunciating his famous distinction between cowboy and spaceship economies: the former associated with limitless plains and associated with the reckless, exploitative and violent behavior that is characteristic of open societies; the second recognizes that the Earth has become a single spaceship, without unlimited reserves of anything, neither for extraction nor for contamination. Therefore, man must find his place in a cyclical ecological system that is capable of continually reproducing material form even though he cannot escape having energy inputs.

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