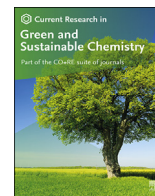


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Synthesis of silica-based solids by sol-gel technique using lemon bio-waste: Juice, peels and ethanolic extract



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ABSTRACT

After the consumption of the edible part, the citrus fruits are thrown into landfills generating serious pollution and disposal problems. Therefore, the use of citrus fruits for engineering applications has a dual purpose: to generate wealth from waste as an efficient reduction of solid waste. The main objective was to obtain silica-based materials from the precursor (TEOS), replacing acetic acid in acid hydrolysis with different parts of a lemon: peel, juice and peel ethanolic extract.

The solids obtained were characterized with different techniques such as TEM, SEM, FT-IR, potentiometric titration and XRD. TEM and SEM images were compared with the synthesized pure silica to contrast the morphology of the acidic hydrolysis with lemon. It can be concluded, in general terms, that the proposed objectives have been achieved, since materials were synthesized through a simple and fast method of obtaining, which allowed their inclusion in oxidic matrices. Until now, few attempts have been made to highlight the renewability of reagents used in the synthesis or to incorporate bio-based catalytic processes in larger scales. However, this research contributes to areas of environmentally friendly materials and synthesis, due to the synthesized solids could be used as a support in eco-catalysts.

1. Introduction

In a Circular Economy (CE), products should be used as long as possible until the end of their shelf life. Modern circularity thinking includes the design of products with adapted lifetime, reusability, ease of repair, and recycling ability—all made with renewable resources [1]. The development and implementation of CE approaches in China [2], United States [3], the European Union [4] and other countries [5] are supported by international organizations such as the World Health Organization (WHO) and the United Nations (UN), and the circular economy is driven by a demand from various sectors towards a global sustainability [6].

Instead of an elimination-of-use pattern, resources are used, retrieved, and updated in internal cycles for as long as possible, creating maximum additional value. When there is a circulation of resources in a broader closed cycle, as well as a contribution to the reduction of greenhouse gas emissions, natural systems can be understood as models to provide better

systemic performance. The circular economy, a concept adopted in previous initiatives and several fields [7] can be described as: an industrial system that is restorative or regenerative by intention and design. Replaces the concept of end-of-life with restoration, shifts to the use of renewable energy, eliminates the use of toxic chemicals, which harm reuse and return to the biosphere, and focuses on waste disposal through superior design of materials, products and systems and business models [8–10]. The role that EC plays when considering the fundamental role of the use of agricultural waste implies being aware of environmental challenges. CE works as the paradigm shift by raising issues unresolved by the 12 principles of green chemistry.

Lemon (*Citrus Limon*) is a flowering plant that belong to the Rutaceae family. It is the most produced citrus fruit around the world, after oranges and tangerines and, Argentina, with 1.98 million tons in 2018, is currently the world's largest producer of lemons.

Phytochemical substances are chemical elements that are naturally

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Fig. 1. Citrus limon L. Burm. f

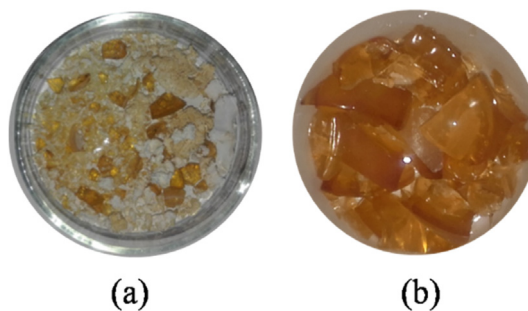
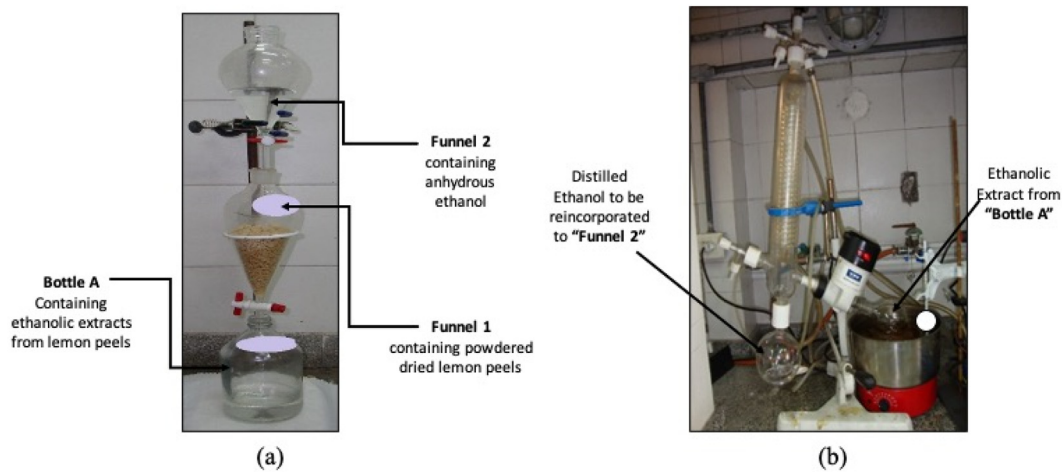


Fig. 3. Photographs of the synthesized solids, a) SLP and b) SLE samples.

Table 1
Textural properties of the synthesized samples.

SAMPLE	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Average pore size (Å)	Desorption BJH average pore size (Å)	t-plot Boer volume of micropores (cm ³ /g)
STA unc	1043.6	0.6	21.1	24.0	0.0
STA c	516.7	0.2	18.4	25.4	0.2
SLJ unc	170.4	0.0	20.6	21.3	0.0
SLJ c	246.9	0.0	20.1	20.1	0.0
SLP unc	121.0	0.1	20.9	0.0	0.0
SLP c	183.4	0.1	25.1	0.1	0.0
SLE unc	121.0	0.1	21.0	0.0	0.0
SLE c	183.4	0.1	25.0	0.0	0.0

unc = un-calcined.
c = calcined.



Scheme 1. (a) Liquid-solid leaching system for powdered dried lemon peels, (b) Rotary evaporation system to obtain ethanolic extracts from powdered dried lemon peels.

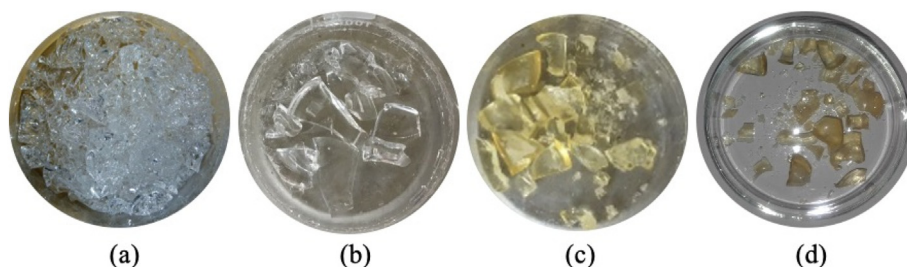


Fig. 2. Formation of vitreous gel with initiation of crystal formation of a) STA sample, b) STA dry vitreous, c) SLJ sample and d) SLJ dry vitreous.

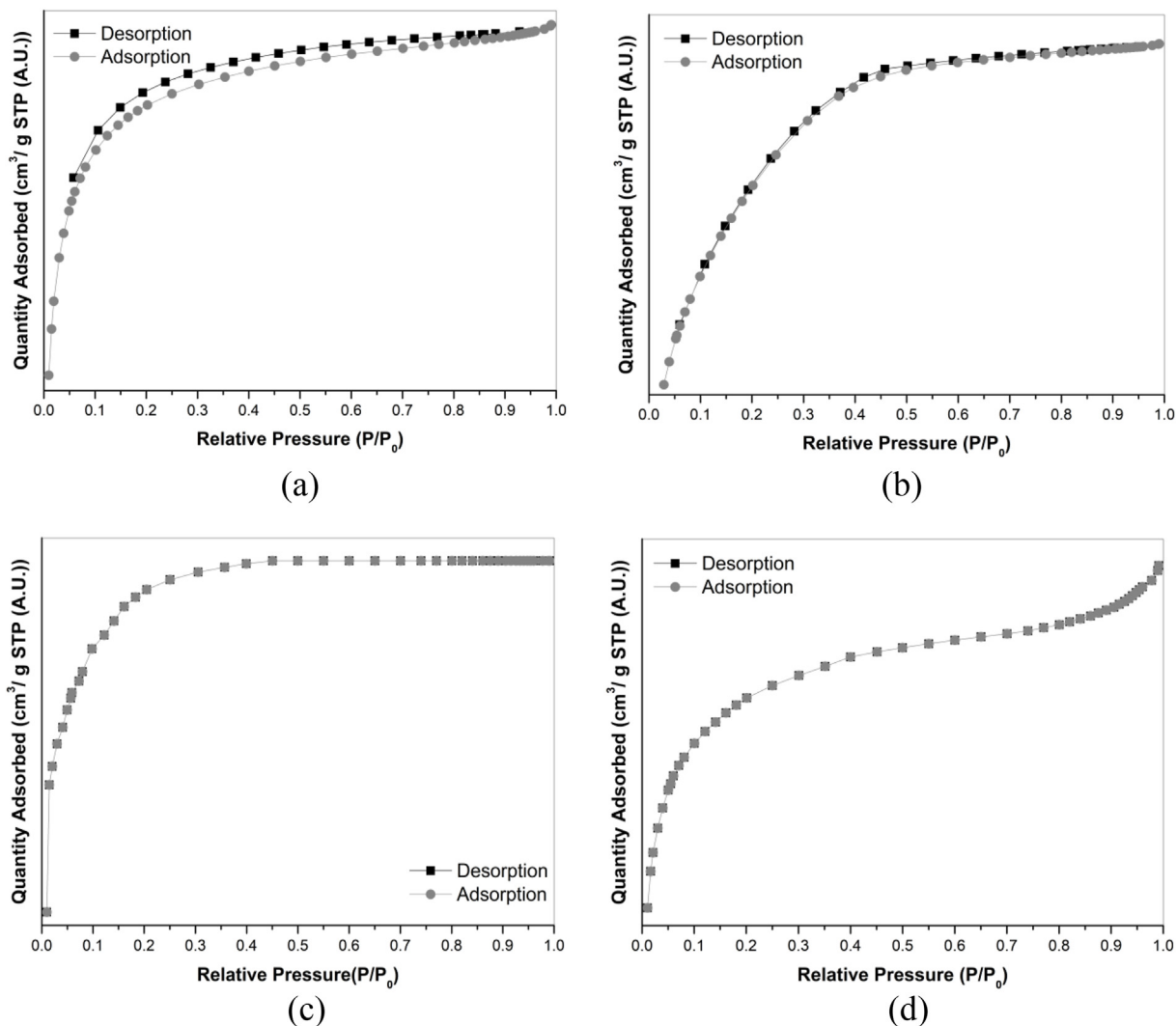


Fig. 4. N₂ adsorption-desorption isotherm obtained for a) calcined STA, b) un-calcined STA, c) calcined SLJ and d) un-calcined SLJ sample.

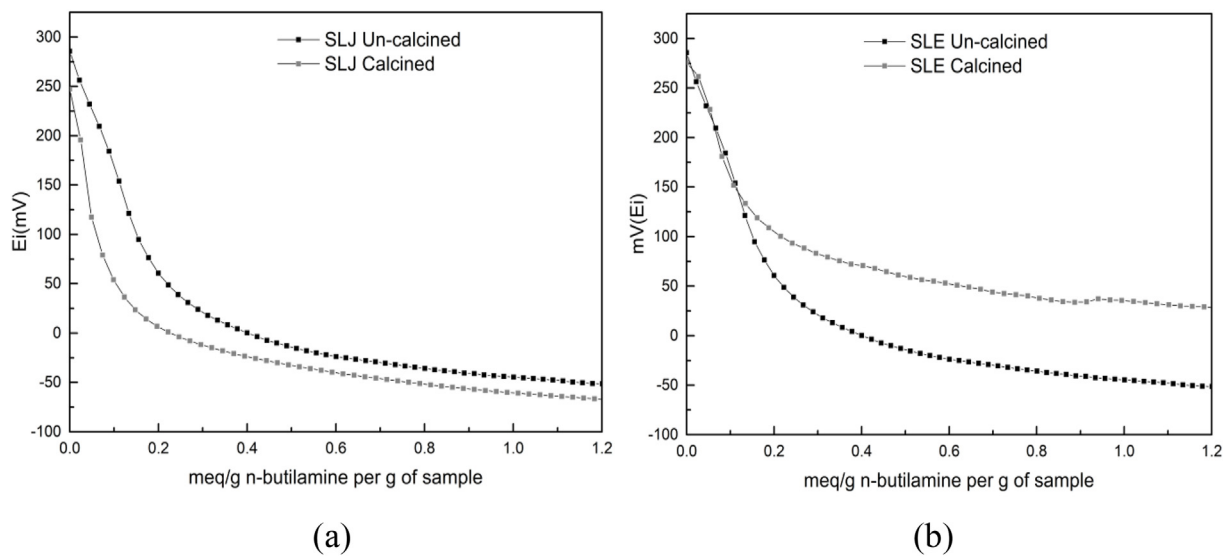


Fig. 5. Potentiometric titration curves of the un-calcined and calcined a) SLJ and b) SLE samples.

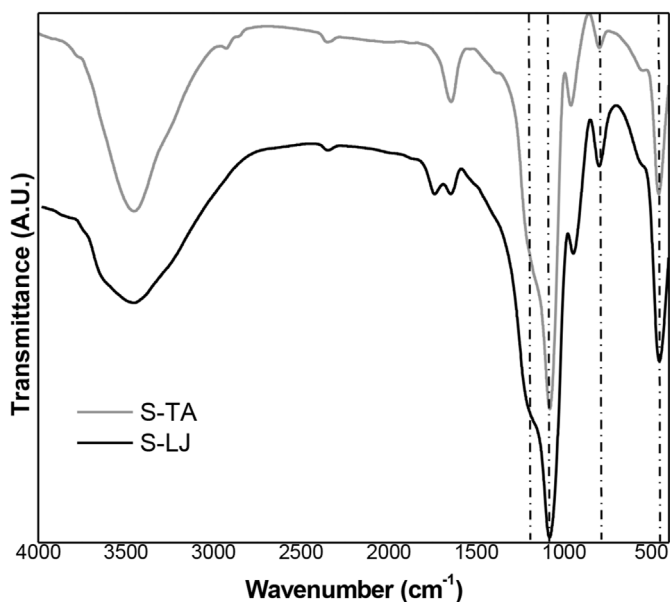


Fig. 6. FTIR spectra of STA and SLJ silica un-calcined samples (Dotted lines: 460, 800, 1080 y 1200 cm^{-1}).

present in food of plant origin. Phytochemicals are found in food but are not properly nutrients, nor macronutrients nor are they included in the vitamin or mineral group. Therefore, they have no energy or nutritional function but are present in certain foods providing various beneficial functions. That is why foods containing phytochemical substances are called functional foods.

There are different ways in which a phytochemical can work: act as an antioxidant and protect cells against the damage of free radicals, for example, polyphenols, carotenoids, etc. Also as an antibacterial component and hormonal stimulant, it can even act as a binder that can prevent pathogen adhesion to the human walls [11]. Phytochemicals are already part of our diet through vegetables and fruits. The citrus fruits are rich in phyto-constituents the citrus limonum (lemon) is one of them [12]. For this work it is important to know that in the citrus limonum the greatest amount of phytochemicals are in the pulp or in the peel [13]. A wide range of compounds could be found in lemon juice and lemon peel. The pulp has carbohydrates, alkaloids, and tannins, fixed oils, reducing sugars, proteins, cardiac glycosides, steroids, phytosterols, phenols and

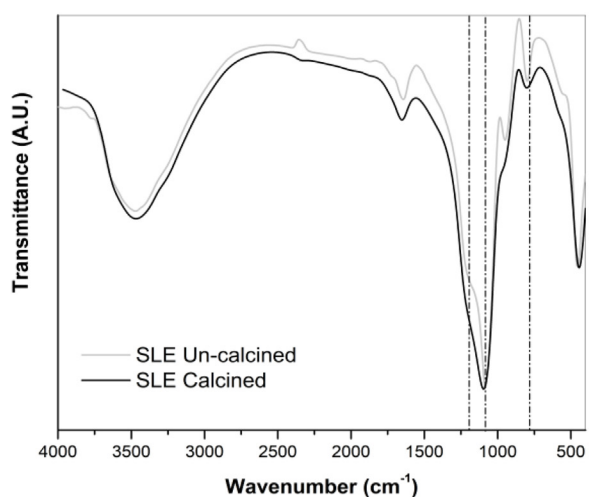
flavonoids. While ethanolic pulp extracts showed only the presence of fixed oils, reducing sugars, cardiac glycosides, steroids, phytosterols, flavonoids and amino acids [14–18]. In citrus, citric acid is the dominant organic acid and generally lemon juice has the highest acidity with over 48 g/L citric acid [19]. Based on there is a difference between the chemical composition of lemon peel and lemon juice. Firstly, the acidity of lemon juice is about 7 times higher than that of the lemon peel solution. This is related to the higher pH value of the lemon peel solution (pH = 4.51) compared to the lemon juice solution (pH = 2.07) [18].

Considering that citrus fruits are cultivated and used worldwide, every year significant amounts of residues such as peels, pulp, fiber and seeds are produced as a result of the productive activities related to these, being able to take advantage of derivatives such as cellulose, lignin, pectin pigments, essential oils, etc., from which until now the pharmaceutical, cosmetic, food and even energy sectors have benefited.

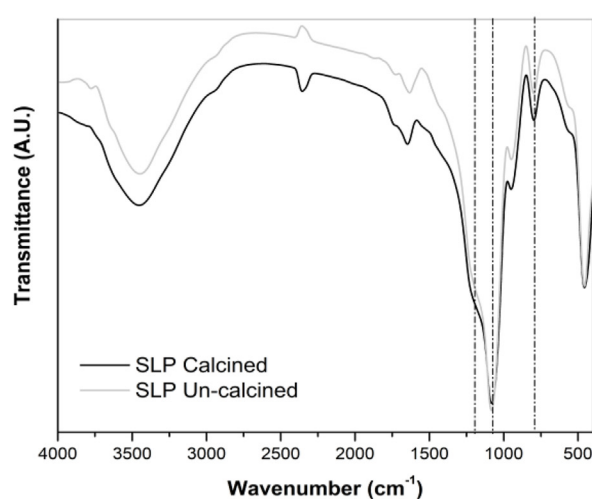
Organic agriculture has remained a haven against the invasion of agro-chemicals and industrialization in the food supply chain [20,21]. It represents less than 1% of global agriculture, specifically reported as 0.98% by the study of Willer and Lernoud (2019) [22]. On the contrary, agriculture is the fastest growing food sector in the world [23]. South America has a strong presence [24–27]. Agriculture wastes are considered a good starting point to discover for new drugs all over the world. In this context, Agriculture wastes contain millions of compounds to be screened to find bioactive compounds responsible for the activity to be used in drugs. Citrus agriculture is one of the most important commercial and industrial agricultural activities in the world. The peel waste of Citrus species is a rich source of bioactive compounds such as essential oils, flavones, polyphenols, and pigment. Citrus peel has been widely used in the medicine industry. The waste peel of citrus consider a rich source of pharmacologically active metabolites with antioxidant activities [28].

Considering this scenario, different investigations propose the use of waste and bio-waste in order to obtain new silica-based materials [27, 29–34]. In according to Pattel et al. [32], agricultural waste is one of the cheapest source for silica production. It contains 50%–90% of SiO_2 . The reasons which are responsible for agricultural waste to be considered as good silica source and have potential for the large scale production are [35,36]:

1. Low cost of the raw material
2. High silica content in agricultural waste
3. Comparable silica quality
4. High energy content



(a)



(b)

Fig. 7. FTIR spectra of a) SLE and b) SLP samples.

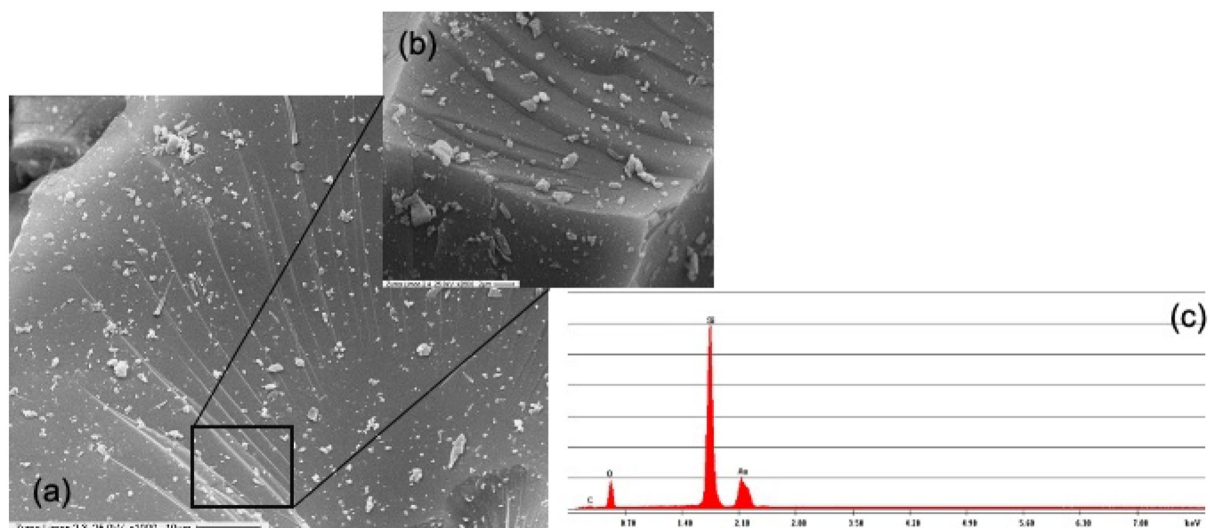


Fig. 8. a) SEM micrographs of un-calcined SLJ sample x1000 and b) x2500 c) EDS SLJ sample un-calcined.

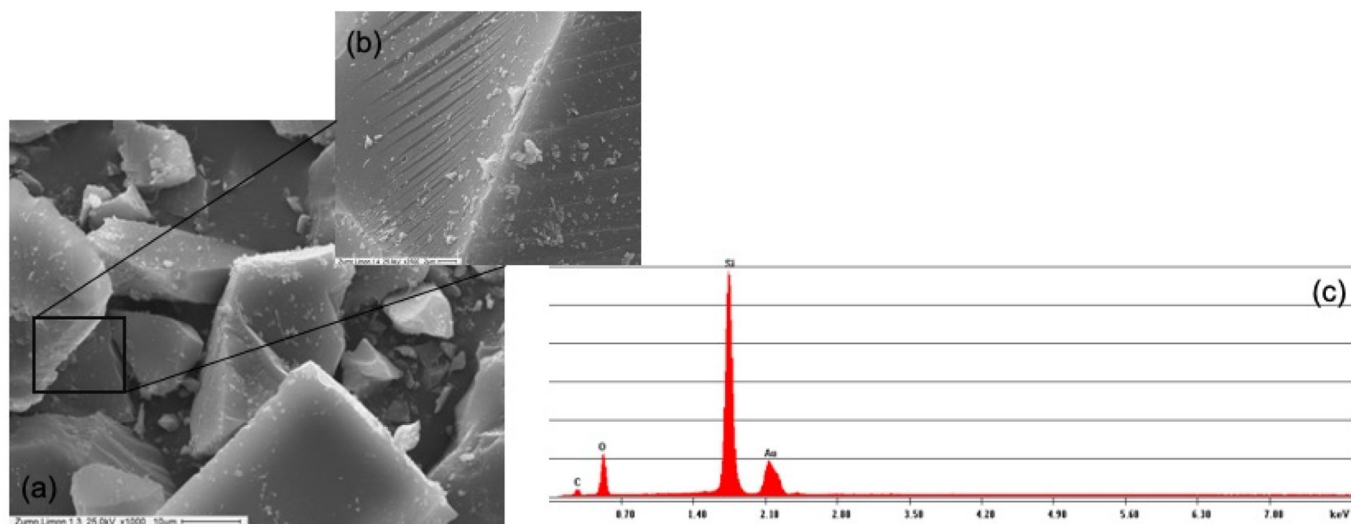


Fig. 9. a) SEM micrographs of calcined SLJ sample x1000 and b) x2500 c) EDS SLJ sample calcined.

5. Fine sized amorphous material

Scientists found many extraction techniques exist for the preparation of amorphous silica from agricultural waste stream. Chemical methods include alkaline extraction method used to produce pure and high amount of silica but it is expensive because of significant longer reaction time (24–48 h), and also requires various steps with the use of various types of chemicals. For example, developed pure silica from rice husk ash with minimal mineral contaminants by using alkaline extraction followed by acid precipitation [37].

In the case of sol-gel technique to obtain silica in contrast to the other techniques, it is important to differentiate their stages. Firstly, a sol is formed. This system is a colloidal dispersion and is called a 'hydrosol' when the liquid medium is water and an 'alcosol' if it is an alcohol [38]. Colloidal solutions or sols contain either large macromolecules, molecular aggregates or small particles, and occupy an intermediate position between true solutions of low molecular weight species and low dispersions. Secondly, a gel is obtained. This solid consists of at least two phases: a solid phase that forms a network that traps and immobilizes a liquid phase [38] formed by the gradual loss of part of the liquid from the sol by evaporation. Hydrosols give rise to hydrogels and alcosols to

alcosols. A polymer gel is an infinite macromolecular network, which is swollen by solvent, and can be created when the concentration of the dispersed species increases. After the sol-gel transition, the solvent phase is removed from the pores of the interconnected network. If removed by evaporation under normal conditions, the result is a xerogel. If stirred under supercritical pressure and temperature conditions, the result is an aerogel.

On the other hand, the gelation time is defined as that in which the sol becomes a gel and is capable of withstanding an elastic stress. Gelation can occur after the sol is introduced into a container, and in this way it is possible to obtain materials with a desired shape. Gelation can occur due to rapid evaporation of the solvent.

The term aging applies to the process of change in structure and properties after gelation. This process may involve continued condensation, dissolution and re-precipitation of monomers or oligomers or phase transformation within the solid or liquid phases. Some gels have a spontaneous shrinkage, known as syneresis, product of the formation of bonds or attraction between particles that cause the expulsion of liquid through the pores [38].

The term "sol-gel" is widely applied to describe the chemical route for the synthesis of inorganic oxides in a relatively simple way. The

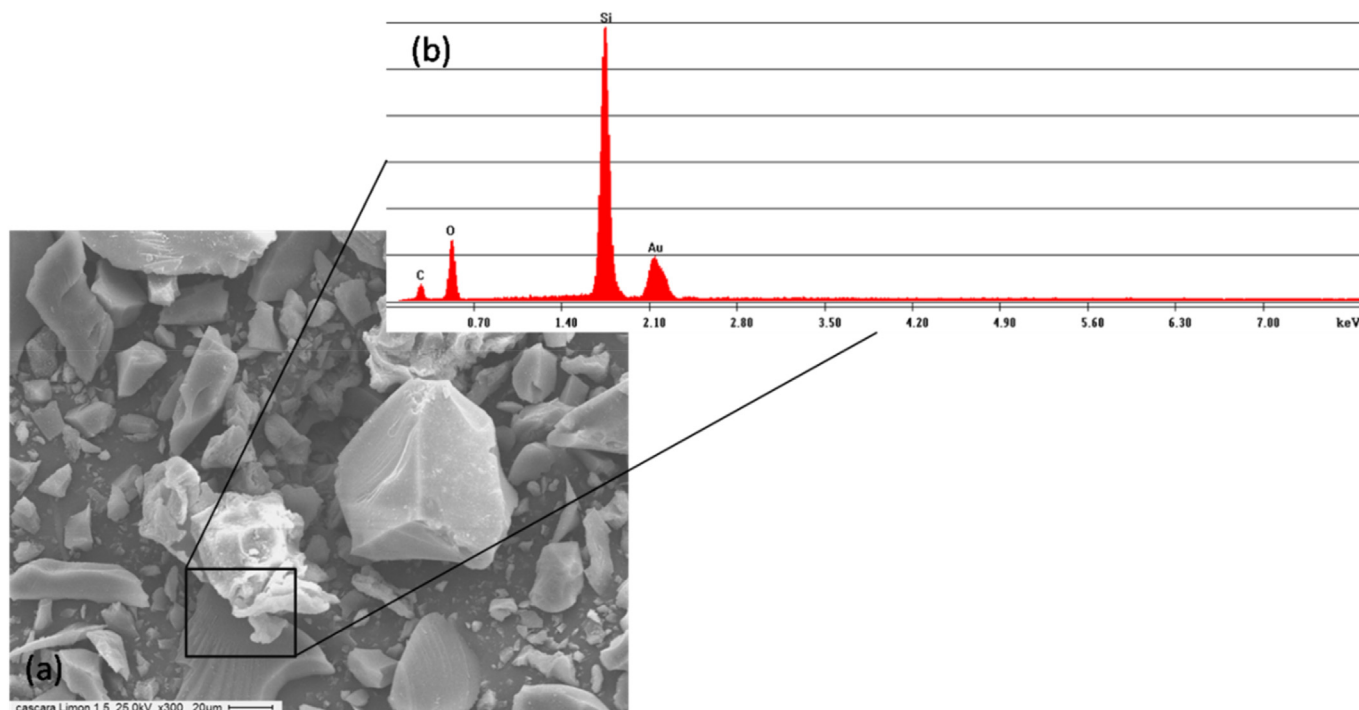


Fig. 10. a) SEM micrographs of calcined SLP sample x300 and b) EDS SLP sample calcined.

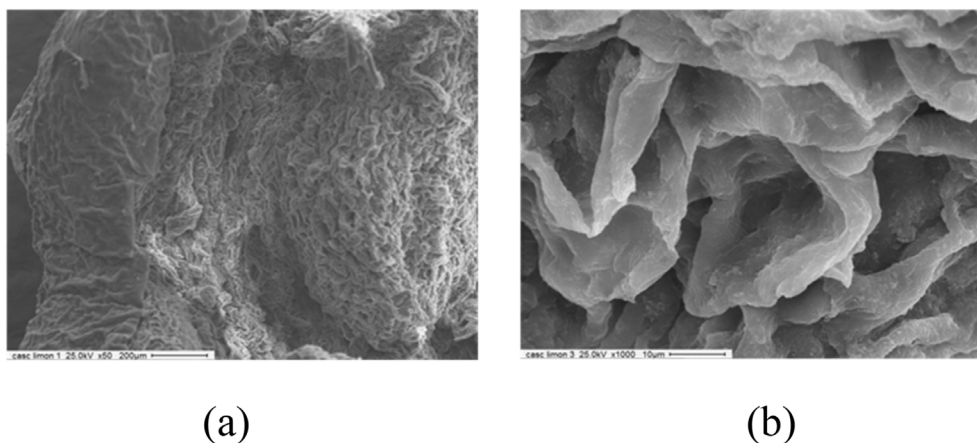


Fig. 11. SEM micrographs of natural lemon peel a) x50 and b) x1000.

development of the sol-gel process has been focused on obtaining oxides and a great variety of materials by processing them at low temperatures.

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 renewability [39,40]. 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 solubilities that participate in the condensation reaction, and with lemon peels, extracting compounds of interest from them [41,42].

In the context of this work, solids were synthesized whose active phase is constituted by silicon oxides and interacting with the citrus molecules present in the fruit matrices. They were added as raw material of the lemon: peel, juice and ethanol extract (exhaustive extraction by ethanolic leaching). To obtain the hybrid materials based on silica, lemons from the City of La Plata (Argentina) were used, mainly taking into account their availability in the region. All synthesized solids were in-depth characterized integrating different physical-chemical techniques, such as Scanning Electron Microscopy (SEM), Transmission

Electron Microscopy (TEM) and Ray-X Diffraction (XRD); Fourier Transform Infrared Spectroscopy (FT-IR), acidic properties by n-butylamine potentiometric titration and textural properties.

The specific objective is the introduction in the sol-gel synthesis of silica matrices with the bio-residues of lemon (peel, juice, ethanol extract) to obtain a support that contains properties that imply the reduction of the use of an active phase or a commercially sourced pore former.

2. Experimental

2.1. Synthesis of materials by sol-gel method

2.1.1. Synthesis of pure silica

For the synthesis of the pure silica (STA sample) the following molar amounts were used, 150 mmol of TEOS, 174 mmol of glacial acetic acid (AcH), 745 mmol of absolute ethanol (EtOH) and 555 mmol of distilled water (H₂O). The synthesis procedure was carried out in a chamber with

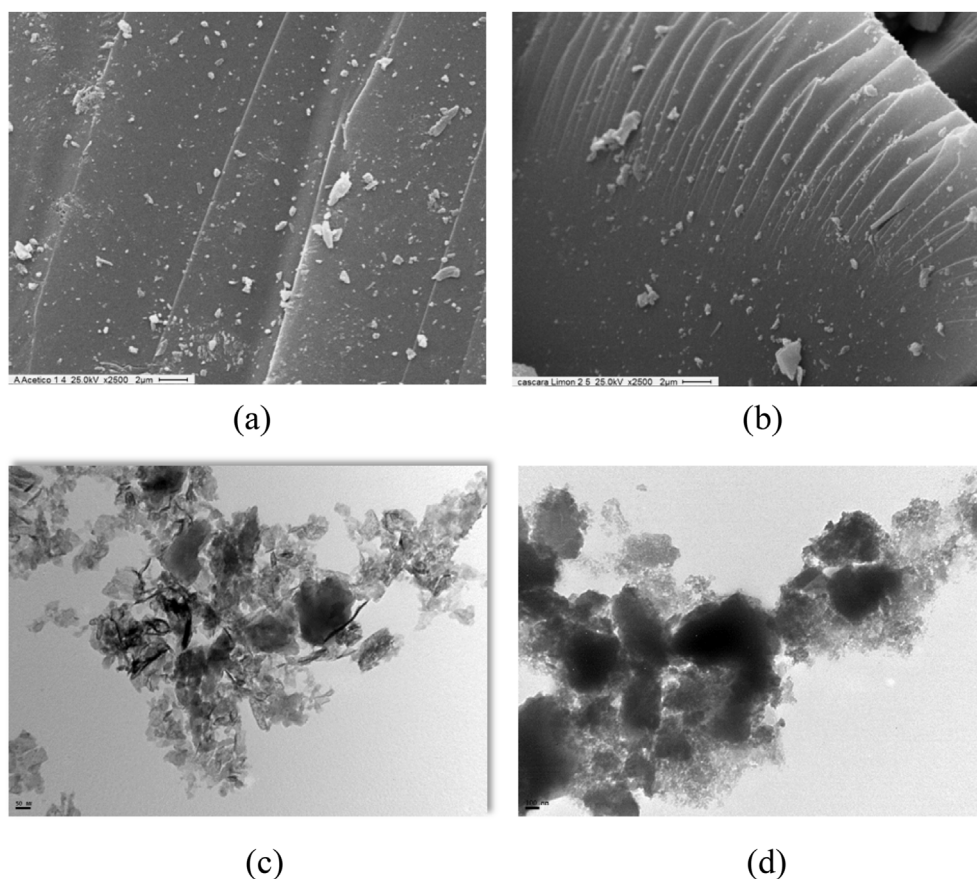


Fig. 12. SEM micrographs of un-calcined samples, a) STA and b) SLP, and TEM micrographs of c) STA and d) SLP samples (Bar: 10 nm).

a controlled nitrogen atmosphere (Atmosbag glove bag®) at room temperature. A portion of absolute ethanol (30 ml) and 10 ml of acetic acid were placed in a beaker and then, TEOS (34 ml), the last portion of the solvent (13.5 ml) and 10 ml of distilled water were added. Subsequently, the reaction mixture was removed from the chamber and work continued under room conditions. The mixed was placed on a magnetic stirring for 2 h at 500 rpm and, the wet was left ageing, at room temperature and atmospheric pressure, until obtaining dry silica particles. Finally, the sample was calcined at 150 °C for 1 h. The sample was placed in a brown bottle for storage.

2.1.2. Synthesis of silica with bio waste

In order to select the characteristics of the lemons to be used, it is important to explain that the customs and habits of consumers were taken into account. Lemons generally are bought voluminous and shiny (freshly harvested) or kept refrigerated. As the lemon is displayed in the market, its skin lose the shine due to the water loss and its volume decreases. This means that in most stores, after a week, the lemons must be removed. Thus, the lemon at 20 days is a residue, from the commercial point of view, as well as its internal modification. To obtain the hybrid materials based on silica, the lemons were used after 20 days from detached from the tree, which would be equivalent to using waste from markets and cities.

Lemons (*Citrus limon* L. Burm. f) were used for this work, grown in the city of La Plata, Buenos Aires (Argentina) [43,44]. According to the latest investigations, it could be a direct crossing between Amargo and Citro Naranja (it is a shrub of the Rutaceas family cultivated by its fruit that has different names: Cidra, Limón Poncil, French lemon or grapefruit, among others). The origin of lemon is a mystery but could come from China, India or Northern Burma. The lemon is a large to large tree, with an open growth habit. Its branches have small thorns and is sensitive

to cold. It has large flowers, intense purple petals. The leaves are pale green that give off a pleasant lemon aroma when they are squeezed. The fruit is light yellow, ellipsoidal, with smooth or slightly rough cortex; it has yellow pulp, juicy and very acidic. The center of the fruit is semi-solid or solid (Fig. 1).

Taking advantage of the complex availability of biomolecules and the diverse level of acidity of the plant tissues present in the lemon, we proceeded to use lemons whose average weight per unit ranged between 100 and 125 g, respectively. To achieve different variables in the acid hydrolysis of the samples of synthesized silica material, it was decided to replace acetic acid with different parts of the lemon: Lemon Juice (LJ), Lemon Peel (LP) and Leach Lemon Peel Ethanolic Extract (LPEE)

2.1.2.1. Lemon juice sample. To synthesized the lemon juice silica (SLJ sample), 15 lemons were cut transversely with a stainless steel knife (300 mm blade) and the extraction and filtration of their juice were carried out. The peel separated during the extraction process was discarded. Filtration was carried out in a glass funnel, by gravity, using grade 1 filter paper. The juice squeezed from the lemons was 200 ml and kept in a brown bottle. The synthesis process, using the obtained lemon juice, is the same as for the pure silica synthesis. Only instead of 174 mmol of glacial acetic acid, 3.0 g of extracted lemon juice (LJ) were used. The nomenclature used to identify the sample was the following: S: silica; lemon juice (LJ), for which the sample will be called SLJ.

2.1.2.2. Lemon peel sample. For the synthesis (SLP sample), 300 g of lemon peels were used. The peels were cut into thin slices (10 cm), then into strips (5 cm long) and finally, were cut into 2 mm by 2 mm cubes. The synthesis process, using the obtained lemon peels, is the same as for the pure silica synthesis, but instead of 174 mmol of glacial acetic acid, 3.0 g of fresh lemon peels (LP) were used.

2.1.2.3. Leach Lemon Peel Ethanolic Extract (LPEE). 200 g of cut into cubes lemon peels were evenly placed on a metal tray for drying in an oven, with recirculation of air at 40 °C, for 15 days. This temperature was chosen only to eliminate the peels humidity. They lost a significant amount of weight in the drying process (approx. 50%), and were subsequently grinded. 100 g of dry powdered peels were obtained. Scheme 1a describes the technique of leaching by the dried husks. This solid was packed in a 500 ml separatory funnel (Funnel 1). A second 500 ml separatory funnel (Funnel 2) was installed in the upper mouth of Funnel 1, containing absolute ethanol. This was done to carry out a liquid-solid leaching of all the substances that could be eluted by anhydrous ethanol. At the stem outlet of Funnel 1, a 1000 ml glass bottle (Bottle A) was placed to collect the resulting ethanol extracts. Subsequently, a reduced pressure rotary distillation of the leachate resulting from Funnel 1 was started when Bottle A was filled (Scheme 1a). The distillation of this liquid was carried out using an oil bath, at 50 °C, with rotation of 70 rpm, vacuum of 12 mmHg and an isopropyl alcohol bath at 4 °C. The ethanol distilled and obtained from the rotary evaporator was incorporated into the leaching system for the second time, filling Funnel 2 again (Scheme 1b). This was carried out until the liquid emanating from Funnel 1 had no coloration, for approx. 15 days. The leached liquid fractions that were collected during each stage in the rotary evaporator (Bottle B), until the extraction process was completed. The leachate fractions were poured into a 500 ml porcelain capsule and subjected to a water bath (8 h) to evaporate all the ethanol present in the extract. Once a viscous paste was obtained, it was placed in a container (Bottle C, caramel color), with a capacity of 200 ml. The solid obtained, containing all the substances extracted with ethanol from the powdered dried lemon peels, was called SLE. The synthesis process, using the viscous paste from lemon peels is the same as for the pure silica synthesis. Instead of 174 mmol of glacial acetic acid, 2.8 g of LPEE were used.

2.2. Characterization of the solids

The textural properties of the solids, such as the specific surface area (SBET), the pore volume and pore size, were determined by adsorption/desorption in Micromeritics Accusorb 2100 equipment (USA), using N₂ as absorbable gas. Before the measurement, each sample was degassed at 100 °C for 12 h. The evaluation of the acidic properties of solids was carried out by potentiometric titration with n-butylamine, in a Metrohm 794 Basic Titrimo titrator (Switzerland), with a double-junction electrode. 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, keeping the stirring time, before to add the first drop, constant (540 s) and a waiting time of the drop of 60 s, while stirring constantly. FT-IR (Fourier transform infrared spectroscopy) spectra were obtained using Bruker IFS 66 equipment (Germany) and pellets of the sample in KBr, at room temperature, measured in a range between 400 and 4000 cm⁻¹. Scanning electron microscopy (SEM) was carried out to obtain different micrographs of the solids, in JEOL equipment, JSM-6390LV (Japan), using a voltage of 20 kV. Samples were supported on graphite and metallized with a sputtered gold film. TEM (Transmission electron microscopy) measurements were performed on a JEOL (model JEM 2011) instrument, operated at an accelerating voltage of 120 kV. Samples were prepared by their suspension in Milli-Q water and placing 5 µL over carbon-coated copper grids, allowing the samples to dry in a desiccator for 16 h at room temperature.

3. Results and discussion

Citrus fruits are of great commercial importance for both the agricultural and exports sector. As for the industrial, food and perfumeries sector. In this context, most citrus production in Argentina is intended for fresh fruit trade, obtaining concentrated juices, frozen pulp, essential oils and dehydrated shell [45].

Citric acid, some malic acid and traces of oxalic predominate in lemon

juice, representing 60–70% of soluble solids. Free acids constitute about 90% of total acids [46]. In this research, the fruits were used 20 days after being cut from the plant, which is equivalent to an external and internal transformation of the lemon, as mentioned above. Many of the properties that are linked to health can disappear for this reason.

Gholipour and Rahimi-Nasrabadi [47] synthesized barium monoferrite nanoparticles have been successfully synthesized via a simple sol-gel auto-combustion method, using lemon juice. The synthesis was based on the reaction between Ba(NO₃)₂ and Fe(NO₃)₃ in aqueous medium, in present of lemon juice as surfactant and fuel agent. Effects of lemon juice amount and the temperature have been investigated to achieve an optimal condition. It was found that the phase and morphology of products could be seriously influenced by these parameters.

Accelerating utilization and recycling of waste volumes to produce valuable biomaterials is a significant research interest worldwide [48, 49]. Palakurthy et al. [50], were used egg shells and rice husk ash (RHA) bio-wastes were used as sources of calcium oxide (CaO) and silica (SiO₂), respectively. Glass samples were obtained by melt-quenching technique. The formation of hydroxyapatite was characterized by XRD. The washed rice husk was treated with 0.5 M concentration of hot hydrochloric acid at ~60 °C for half an hour under constant stirring. After removing the acid solution, the rice was rinsed with distilled water until it was free from acids.

In our previous research [51], the main objective was to obtain silica-based materials from TEOS with different catalysts (acetic, citric and hydro-chloric acids and ammonium hydroxide) adding different percentages of lemon and orange peels in order to find the influence of bio-waste on acids/alkali precursor hydrolysis. This was to partially replace these catalysts for orange or lemon peels. The solids obtained were characterized with different techniques. SEM images were compared with pure silica obtained to contrast the morphology of the acidic and alkali hydrolysis. The sol-gel technique is the green synthesis of silica materials.

In Fig. 2, the photographic records of the solids obtained are shown, using TEOS as precursor and acetic acid as catalyst (Fig. 2a and b) and lemon juice (Fig. 2c and d). A similarity can be observed in the morphology of the gel obtained with lemon juice (SLJ) with the gel obtained with acetic acid (STA), which implies acid hydrolysis due to the pH of the synthesis. Obviously, the coloring of the vitreous gel obtained with lemon juice (Fig. 2d) compared to the STA sample obtained with acetic acid (Fig. 2b) is different. This is due to the lemon juice coloring, which is slightly yellowish.

In most cases a catalyst (acid or base) is used, since water and alkoxide do not mix, an alcohol is used as a solvent. In this case, the lemon juice solubilizes better than an alkoxide. In the hydrolysis reaction, the replacement of an alkoxide group (OR) takes place by a hydroxyl group (OH-). Subsequently, the condensation reactions, which involve the silanol groups (Si-OH), produce siloxane bonds (Si-O-Si) and as by-products alcohol (ROH) or water [52].

The condensation begins as soon as the alkoxy groups hydrolyze. The initial condensation rate is very high and short chains (or oligomers) are formed at this stage. In a later state, further condensation is possible only through crosslinking of the formed chains. These chains are separated, one from another, by alcohols and water molecules. Crosslinking of these chains leads to the formation of a gel [53].

In the sol-gel process, dimers and trimers are rapidly formed, condensed into cyclic siloxane units (Si-O-Si); these mainly contain four or six silicon atoms. It is also consistent with the assumption that the polymerization process is controlled by the formation of silica dimers as long as the solution is supersaturated. These dimers are formed by the condensation of monomeric silica, which forms high molecular weight polymers [54-57].

The concentrations of terminal -OH and/or -OR groups depend on the kinetics and mechanisms of hydrolysis and condensation, particularly determined by the nature of the applied catalyst [41].

No studies were performed on the kinetics of lemon juice hydrolysis. For this reason it can only be compared with studies of acid hydrolysis such as acetic acid as used in pure silica synthesis. At this point, it is interesting to compare the gelation when the hydrolysis has already been carried out. Gelation is physically manifested by a drastic increase in the viscosity of the solution [58].

These changes in viscosity occur without any generation of chemical transformations or endothermic or exothermic changes [59,60].

The wet gel can be strengthened by aging and by syneresis mechanism Ostwald maturation [61,62]. The syneresis is characterized by the contraction of the gel network, produced by the expulsion or extraction of liquid. The gel that is a homogeneous substance becomes a segregation of solid components. Smaller particles have a higher solubility, which leads to their precipitation and the formation of larger ones [63].

During drying, the effect of citrus peels on the surface of the solids obtained indicates that the silicon skeleton becomes increasingly rigid. When the surface tension cannot deform the network, the gel body becomes too stiff. At this point, the likelihood of it breaking is higher [64, 65].

Fig. 3 shows the photograph of the vitreous gel of the SLP sample obtained with lemon peel instead of acetic acid as a catalyst and, SLE sample obtained with lemon ethanolic extract. A similarity can be observed in the morphology of the gel obtained with lemon juice (Fig. 2), which implies acid hydrolysis due to the pH of the synthesis. The staining of the SLP gel is similar to that of the SLJ sample, but without being homogeneous. This could be due to the presence of solid compounds in the SLP sample with lemon peel. In SLE sample, different solids, glassy and non-glassy, were obtained with a strong orange color from the ethanolic extract. This implies that a siliceous gel was not obtained, only a mixture of solids based on silica. It could be said that the hydrolysis of the synthesis was not acidic like the previous ones and probably the compounds were not sufficiently basic to obtain silica.

The textural properties of the synthesized samples are presented in Table 1. The Brunauer-Emmet-Teller (BET) method is the most widely used and accepted standard procedure for the determination of surface areas of a wide range of fine powders and porous materials. According to the values obtained for S_{BET} , the SLJ sample has a behavior that could be assimilated to a greater loss of liquid (lemon juice) in the calcined sample, which implies an increase in surface area. The value of the average pore size for the un-calcined and calcined SLJ remain at similar values and the pore volume for both samples, obtained by different measurement techniques, presents a value approx. to $0 \text{ cm}^3/\text{g}$. If the STA and SLP specific surfaces values were compared, it can be seen that the un-calcined STA sample has a value of $1043.6 \text{ m}^2/\text{g}$ that decreases to $121.0 \text{ m}^2/\text{g}$ and, the calcined one of $516.7 \text{ m}^2/\text{g}$ decreases to $183.4 \text{ m}^2/\text{g}$, respectively. This change may be because the lemon peel added to the synthesis is a mixture of solid-liquid consistency, which could be interpreted as a percentage of loss of the liquid phase due to the incorporation of the lemon peel. The little amount of liquid phase can be relocated in the siliceous network, but occluding the pores of the silica skeleton when gelation begins.

Fig. 4 shows the N_2 adsorption-desorption curves of the STA and SLJ samples, un-calcined and calcined, respectively. The calcined SLJ sample (Fig. 4c) can be considered a Type I, the isotherm is concave with respect to the relative pressure axis (p/p_0), increases rapidly at low pressure ($p/p_0 < 10^{-3}$) and subsequently reaches a horizontal saturation plateau. This type of isotherms is characteristic of microporous materials (mean pore diameter less than 2 nm). It can be seen that both isotherms present a long plateau, very similar to the calcined silica obtained with acetic acid [66]. The un-calcined SLJ sample (Fig. 4d) can be considered Type II. These isotherms at low pressures are concave with respect to the relative pressure axis (p/p_0), then it increases linearly and finally becomes convex. It can be interpreted as the formation of an adsorbed layer whose thickness is progressively increased as the pressure increases. This would indicate that the behavior of citric acid, in lemon juice, reacts in a similar way with TEOS. The N_2 adsorption-desorption curve of the un-calcined

SLP sample was Type I (similar to STA), while the isotherm of SLP calcined belongs to Type IV with hysteresis loop, respectively. It could be thought that the sample synthesized with peels conserves enough liquid before being calcined and therefore when it is calcined has a greater quantity of solid in its structure. The low surface area is possibly due to the operational complexity of degassing lignocellulosic samples [67]. Furthermore, low surface area is a characteristic feature of carbonaceous materials [68].

For potentiometric titration with n-butylamine of the un-calcined SLJ sample, the E_i value is 287.0 mV and decreases to 247.2 mV when the sample is calcined. It can be deduced that only water or ethanol is lost in wet gelation during calcination. It could be assumed that the lemon juice would need a higher temperature to show a change in the acidity of the gel and therefore there would be an indicator of a lower acidity in the calcined sample. Fig. 5a shows that in the calcined SLJ sample, the amount of acid sites decreases by almost half that of the un-calcined sample, which indicates the existence of sites with less acidity in both samples. For the un-calcined SLP sample, the E_i value is 225.4 mV and decreases to 191.1 mV when the sample is calcined, showing that only water or ethanol is lost from the wet gelling mixture on calcination. Fig. 5b shows that in calcined SLP sample, the amount of acid sites decreases almost to half that of the un-calcined sample. But the plateau begins, respect to the un-calcined SLP sample, at a value of 0.6 meq/g. Indicating the existence of sites with lower acidity in both samples.

FT-IR is one of the most common spectroscopic techniques used to determine the chemical functional groups of a solid sample [69,70]. In Fig. 6 the spectra of the un-calcined SLJ sample and the spectrum of pure silica are presented [66], both samples un-calcined. When we analyze the spectra at lower values of wavenumbers, four well defined bands: at 460, 800, and 1080 and around 1200 cm^{-1} are observed (dotted lines) corresponding to vibrations of silicon-oxygen bonds. And can be classified by the type of movement of the oxygen atom respect to the silicon atoms in balancing, bending and stretching [71]. Those bands are typical of SiO_2 and systematically appear in these kind of materials.

Bands at 1200 and 1080 cm^{-1} are assigned to asymmetric stretching modes of Si-O-Si bonds and the vibration at 800 cm^{-1} is associated with the symmetric stretching of the Si-O-Si bond or vibrational modes of ring structures. At the lower wavenumber value, the band at 460 cm^{-1} is assigned to the bending mode of the Si-O-Si, although it can be associated with defects caused by non-symmetric bond. The band located around 560 cm^{-1} is attributed to the deformation of four-membered siloxane rings (cyclotetrasiloxanes). Because cyclotetrasiloxanes are stable during hydrolysis processes, they can constitute a large fraction of the oligomeric species present in TEOS-derived systems [72]. FT-IR spectrum allows to observe a broad band around 3400 cm^{-1} assigned to the symmetric stretching of OH bonds corresponding to physically adsorbed water on the solid. The signal at 1640 cm^{-1} is attributed to bending OH vibrations of water molecules in the solid retained by hydrogen bonds [73]. The presence of these two bands indicates that the xerogel silica contains a high amount of molecular water and hydroxyls. Finally, the band centered around 950 cm^{-1} is assigned to the vibration of Si-OH bonds (silanols) [74,75].

The main absorption peaks observed are associated with the vibration modes of the Si-O-Si bonds. It can be seen that the spectrum of un-calcined SLJ is very similar to that of STA silica, under the same conditions. It could be said that along with the vibration mode of the Si-O-Si bonds of the STA sample, there are other associated vibration modes that move and widen the main band. In the range $1700\text{--}1500 \text{ cm}^{-1}$ corresponding to the SLJ. These associated modes of vibration may correspond to impurities that are adsorbed to the surface of the sample, tightening the Si-O-Si bonds on the surface and causing two bands to appear associated with the same mode but, vibrating with different frequencies. In Fig. 7, the spectra of the un-calcined and calcined SLE and SLP samples are presented. FT-IR spectra of SLE and SLP samples shows the characteristics bands of silica samples.

Regarding the morphology of the SLJ sample un-calcined, Fig. 8

shows the EDS analysis and the SEM micrographs. In EDS, the Si peak can be observed in the majority. It presents a laminar morphology characteristic of acid hydrolysis. Regarding the calcined SLJ sample and SLP sample, Fig. 9 and Fig. 10 respectively, shows the SEM micrographs and the EDS analysis, showing similarity in the results of the un-calcined one.

The outer layer of the lemon peel is called flavedo, whose color differs from green to yellow, flavedo is a rich source of essential oils, which has been used since ancient times in flavoring and fragrance industries. The main component of the lemon peel is the albedo, which is a fluffy, cellulosic layer underneath the flavedo and has a high content of dietary fiber [76]. Among the wastes, fruit peels represent important source of carbohydrates that make them attractive biomass for the production of value-added products such as bacterial cellulose. Citrus peels, not consumed with fruits due to their bitter taste, represent approximately 30–60 g/100 g of the citrus fruit weights [77].

A microscopic observation of lemon peels shows the geometry of the particles and structural variations on the surface of the lemon peel (Fig. 11a and b). The surface of the citrus peel is uneven, rough and contains some fibers. Furthermore, the shape and sizes of the particles are also different. The particles vary in the form of spherical to long scales [78].

The SEM micrographs of STA sample and SLP sample are shown in Fig. 12a and b respectively. TEM micrographs of the STA and SLP samples are shown in Fig. 12c and d. The micrograph shows how the sheets are formed, from lighter to darker, indicating probably the blocks that were visualized in the SEM micrograph. These blocks can be observed in the micrographs corresponding to a scale of 100 nm, where the lighter parts would correspond to the silica from less agglomerated sheets.

The TEM micrographs of the samples are consistent in morphology with the SEM micrographs, with a laminar structure that ranges from slightly agglomerated to dark agglomerates as in the other TEM micrographs.

4. Conclusions

This work meets several points that describes the principles of green chemistry. It can be concluded, in general terms, that the proposed objectives have been achieved, since materials were synthesized through a simple and fast method of obtaining, such as the sol-gel method, which allowed their inclusion in oxidic matrices.

Silica was synthesized with acetic acid (STA), acid hydrolysis, and it could be seen that the acidity decreases when the solids obtained are subjected to calcination. Using the different parts of the lemon, it can be observed that the acidity is not only higher than those obtained with acetic acid, but also decreases when each part is subjected (peel, leached peel, along with the other parts), to calcination.

The aging of the wet gel in alcoholic solutions containing the silica precursor causes the hydrolysis, condensation and precipitation of the added monomers/oligomers in the gel network. This process increases the rigidity of the silica network by adding new monomers and improving the degree of siloxane crosslinking, without drastic changes in pore size. Aging wet gel in aqueous solution can promote dissolution and re-precipitation of small silica at the point of contact of the particles, which will increase the neck area and thus improve the skeletal strength of the gel. It increases the mechanical stability of silica gels and leads to a decrease in the external and microporous surface. It should be noted that the high concentration of water in the aging solutions causes a faster contraction and hardening of the gels, this can be observed in the surface areas of the silicas that contain a greater amount of solid organic compounds.

A “green” circular economy was sought by reflecting on the systemic role of chemistry on sustainability. The chemistry necessary for a circular economy will materialize only through a new attitude towards chemistry education, chemical research and engineering, and the design of new products.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

None.

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