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Protocol for Analytical Techniques and Identification of Reusable Silica from Acid Oxidative Purification[*]

Protocolo de Técnicas Analíticas e Identificação de Sílica Reusável Proveniente da Purificação Oxidativa Ácida

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Abstract

Silica gel functions as an adsorbent employed in identification, separation, and purification techniques. It is commonly used to purify organic compounds. The primary objective of this study is to reduce operational expenses associated with the procurement of this compound by facilitating its reuse, thereby aiming to recover the commercial value. The recovery of silica entails a series of purification steps. Silica is roughly washed using water, followed by exhaustive oxidation using potassium permanganate ($KMnO_{4(s)}$) and sulfuric acid (H_2SO_4), vacuum filtration, dried over the oven and sieved. Effectiveness of the treatment was detected by using different methods. Various analytical techniques were employed, such as Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS), Infrared Spectroscopy (IS), Thermogravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC). In summary, the costs associated with the treatment reagents, such as potassium permanganate, concentrated sulfuric acid and sodium oxalate ($Na_2C_2O_{4(s)}$), have demonstrated that the method employed is an economical alternative process that can be done instead of purchasing a new product. The treatment of silica represents a viable alternative, offering a sustainable approach for its reuse.

Keywords: Silica gel. Purification treatments. Exhaustive oxidation. Analysis techniques of characterization. Sustainability.

Resumo

A silica gel funciona como um adsorvente empregado em técnicas de identificação, separação e purificação onde é comumente utilizado para purificar compostos orgânicos. O principal objetivo deste estudo é de reduzir os gastos operacionais associados à aquisição desse composto facilitando sua reutilização. A recuperação de silica é composta por uma série de processos de purificação. O material foi grosseiramente lavado com água, seguido por processos de oxidação exaustiva utilizando permanganato de potássio ($KMnO_{4(s)}$) e ácido sulfúrico (H_2SO_4), filtração a vácuo, secagem na estufa e, por fim, peneiramento. A eficiência do tratamento foi estimada utilizando várias técnicas de análise, como Microscópio Eletrônico de Varredura (MEV), Espectroscopia por Energia Dispersiva de Raio-X (EDS), Espectroscopia de Infravermelho (IV), Análise Termogravimétrica (TGA) além da Calorimetria Exploratória Diferencial (DSC). Em suma, os custos associados aos reagentes utilizados no processo de tratamento, como o permanganato de potássio, ácido sulfúrico concentrado e oxalato de sódio ($Na_2C_2O_{4(s)}$), demonstraram que se trata de um processo econômico alternativo que pode ser realizado ao invés de se comprar o produto novo. Esse tratamento de silica apresenta uma alternativa viável, oferecendo uma abordagem sustentável para o seu reuso.

Palavras-chave: Silica gel. Purificação. Oxidação exaustiva. Técnicas de análise de caracterização. Sustentabilidade.

1 INTRODUCTION

Recycle materials are a growing concern in the modern world. Recovery of metals, plastics and paper are some examples that countries are escalating in recovery. Although, about 96% of the residue produced in Brazil are not reused or are given the correct treatment to be in conditions to be reused (BRASIL, 2019). Additionally, research materials are still consumed on a large scale without any recovery. Consequently, it is necessary to research new purification methods as an alternative for disposing of them without causing concern to the environment. In addition, use of water as solvent in different processes reduces organic waste production.

Silica gel is a white nano powder and absorbent component with marvelous characteristics. Its structure is made by a lattice of silicon and oxygen atoms that are bonded in a 3 dimensional-structure, and it has also hydroxy groups ($-OH$) in its surface nominated silanol groups. The silanol, geminal silanol and siloxane groups at its surface are responsible for most intermolecular interaction with organic compounds. Polar molecules interact strongly with this material during purification processes (MEYER, 2004).

In old times, the major way of silica production was from mining followed by purification to generate a fine particle. Other ways to form silica is by treatment of ashes prevalent from rice (FERNANDES *et al.*, 2017). Different sources of silica are bentonite, sand and diatomaceous earth rice husk that have very small amounts of contaminants. Chemistry laboratories use silica for purification purposes such as chromatography methods. Also, it can be used as a form to dry materials in the lab (VIEIRA *et al.*, 2021; VOGEL; AFONSO, 2022).

This material is also a very common adsorbent and can be utilized to remove moisture from the air. Because of this characteristic some studies have been made, such as its application on process of desalination of water on an adsorption desalination process. Silica gel is able to retain the water vapor, generated from evaporation of sea water during a thermodynamic cycle (THU *et al.*, 2013).

Silica gel generally is commercially available from several Chemical industries and its price can fluctuate depending on the type and amount. However, its price is generally very high. Despite its commercial accessibility, comprehensive information about silica's properties and applications remains limited.

Metallurgical silicon is obtained by silica and to be used in the confection of solar panels, it must pass through a reduction treatment, in a temperature around 1500°C, so it can be used on this function. The conventional procedure responsible to produce metallurgical-grade silicon is called the Siemens process, which involves heating metallurgical silicon with Trichlorosilane gas (TIBURTIUS *et al.*, 2005).

In order to demonstrate effectiveness of purification process, several methods were adopted with silica final product. Scanning Electron Microscopy (SEM) is a device capable of providing information from materials surface (FERREIRA; PEREIRA; NEVES, 2019), it can be used as a means of comparison between two materials. Moreover, Energy Dispersive

X-ray spectroscopy (EDS) is attached in the SEM, and it provides information about the surface composition of the samples (FERREIRA; PEREIRA; NEVES, 2019). Thermogravimetric Analysis (TGA) calculates the mass loss in function of the temperature variation. It gives crucial information about the compound and possible impurities that may be present in the analyte. Moreover, the Differential Scanning Calorimetry (DSC) can also be used as additional information about the energy involving the TGA (LOPES; FASCIO, 2004). Infrared spectroscopy (IR) is a technique that provides important information about functional groups and is very important in characterization of organic molecules (SKOOG; WEST; HOLLER, 2009).

Purification technique of silica should consider a method capable of removing all impurities without modifying silica molecular structure. Also, it should be a cheap and reliable procedure that can be reproduced by any student or technician. Therefore, rinsing silica with tap water and oxidative purification is a simple and interesting way of providing very reliable results. The reaction between potassium permanganate ($KMnO_4$) and organic compounds, as presented in Equation 1, is responsible for carbon-carbon bonds rupture. It produces manganese dioxide (MnO_2), carbon dioxide (CO_2), carboxylic acid, alcohol, potassium salts and nonvolatile intermediary compounds (LEGRINI; OLIVEIROS; BRAUN, 1993).

$$\mathrm{KMnO_4(aq)} + \mathrm{H_2SO_4(aq)} + \mathrm{Impurities} \longrightarrow \mathrm{CO_2(g)} + \mathrm{MnO_2(g)} + \mathrm{K_2SO_4(aq)} + \mathrm{H^+(aq)} \quad (1)$$

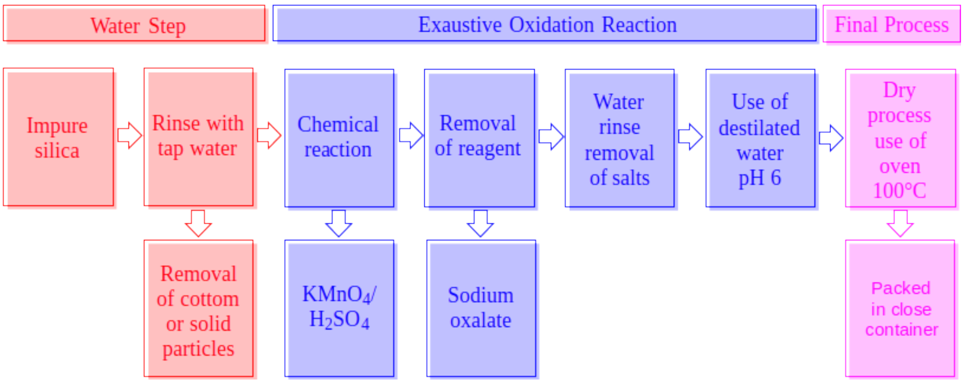
Advanced oxidative processes are capable of efficiently degrading organic substrates by breaking double bonds and generate intermediates. Transitional compounds are unstable and quickly reduced to organic alcohols and carbon dioxide gas. The concept of the process involves oxidation of organic compounds to render them water-soluble compounds. Therefore, removal of impurities is easier to accomplish by washing with tap water (DASH; PATEL; MISHRA, 2008).

2 DEVELOPMENT

2.1 Methodology

Purification methodology involves several steps including mechanical and chemical procedures. The first step requires physical removal of particles. Particles such as cotton, grains and other organic solids from impure silica were removed by thoroughly washing it with tap water until the water was translucent. Once silica is exhaustively washed, chemical reactions can be applied. Then, potassium permanganate and concentrated sulfuric acid were added, and were is vigorously mixed from time to time until the violet color is maintained without any gas production. Usually, this step can take over 72 hours to be accomplished depending on the impurities of silica. Finally, excess of oxidative reagents are removed using sodium oxalate, it was continuously added with concentrated sulfuric acid until the silica turns pinkish white. Afterwards, the silica was thoroughly washed with tap water until all salts are removed. After rinsing with water, the pH of final product was the same as tap water (around pH 6.0). The presence of metal and contaminants in the water then can be removed by rinsing with distilled water. When this is done, the silica is washed a few times, approximately three times, with distilled water. Then it was vacuum filtered and dried in an oven at approximately 100°C for 48 hours to remove water residual. Finally, it is sifted and stocked in a closed container. The scheme shown in Figure 1 is an illustration of the process.

Figure 1 – Flowchart of the treatment of silica gel



Source: Developed by the authors.

In this procedure, starting from 210g of impure silica, it was added 40g of potassium permanganate and 25mL of concentrated sulfuric acid, followed by 40g of oxalate sodium and 20mL of concentrated sulfuric acid and rinsed it with 10L of water. Reagents amount can vary depending on silica purity.

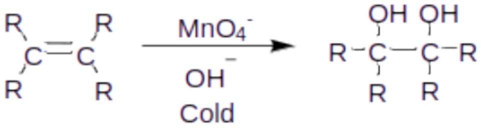
Different methods of silica characterization were applied to certify the purity of silica such as IV spectroscopy, TGA-DSC scanning and SEM-EDS.

2.2 Oxidative Processes

Oxidative processes using potassium permanganate ($KMnO_{4(s)}$) under acidic conditions (achieved by conc. H_2SO_4) are a well-known method of purification (DE MÈO *et al.*, 1991). This technique is also capable of breaking C-C bonds and can be used as an option for removing organic impurities. The oxidative process can be measured by formation of co-products such as MnO_2, CO_2 gas and other substances that may vary due to the presence of organic residues (MAHMOODLU; HASSANIZADEH; HARTOG, 2014).

Potassium Permanganate has some other interesting characteristics that make it possible to be used as an oxidizing agent, such as its high oxidation potential in addition to its ability to be used in wide ranges of pH and its cost (MAHMOODLU; HASSANIZADEH; HARTOG, 2014).

The anion MnO_4^- reacts with the organic substances in acid environment to break the double bonds and form alcohol organic compounds that are soluble in water (DEDAVID; GOMES; MACHADO, 2007). The reaction promotes the rupture of C=C bonds, leading to the formation of organic alcohols, as can be seen in the reaction shown in Equation 2.



(2)

Moreover, the $KMnO_4$ is found as a violet powder that is soluble in water. This compound in acid environments reduces to Mn^{+2} as it can be seen in the reduction half-reaction, shown in Equation 3 (DASH; PATEL; MISHRA, 2008):

$$\mathrm{MnO}_4^-{}_{(aq)} + 8\,\mathrm{H_3O}^+{}_{(aq)} + 5\,e^- \rightarrow \mathrm{Mn}^{+2}{}_{(aq)} + 12\,\mathrm{H_2O}_{(l)} \tag{3}$$

2.3 Scanning Electron Microscopy – Energy Dispersive X-Ray spectroscopy (SEM/EDS)

Scanning Electron Microscopy (SEM) is an important instrument employed to analyze solid compounds' structure, composition, and electrical behavior in nano and micro areas (VERNON-PARRY, 2000). This equipment produces and applies a stable and high energy beam of electrons in the sample. When the beam is out of the electron gun, it has a large diameter, consequently, there are lenses inside of the SEM that reduce it so it will form a high-quality image. This way, the microscopy has detectors that track down different signs caused by the interaction between the electrons and the surface of the sample generating the substance surface representation (MOHAMMED; ABDULLAH, 2018).

The image developed by the SEM has higher resolution than the other microscopes because its beams get to the core of the surface atoms and, consequently, it has higher interactions with the sample. Besides that, this microscopy has secondary beams formed by the compound's electrons that are ejected when the primary beams get in contact with the substance. Secondary beams have lower speed than the primary ones, but they also interact with surface and are tracked down by the detectors, which means they help to form the final representation as well (MOHAMMED; ABDULLAH, 2018).

Therefore, the image formed by SEM of the treated sample should have a similar pattern to the commercial one since both have the same substance (silica gel). However, the used silica before treatment has on its composition organic impurities including organic molecules and/or solvents caused by its use in the laboratory. Because of that, its surface and, consequently, its representation are different from the other samples.

Attached to the SEM, the energy dispersive X-Ray spectroscopy (EDS) is a technique that provides information about the chemical composition of the sample's surface, this method consists of the emission and interpretation of characteristic X-ray photons (DEDAVID; GO-

MES; MACHADO, 2007). In this case, the high energy beam of electrons can cause the loss of one of the most internal shell electrons on the atom, this gap then can be filled with another electron from a more energetic shell (VIEIRA *et al.*, 2021). Moreover, this electronic transition is characterized by an emission of a specific X-ray, that is unique for every element, and it can be detected by the equipment and generate a spectrum that can be used in the interpretation of the composition on the surface (VIEIRA *et al.*, 2021).

Elements can be identified from the peak of energy on the spectrum once every element has a characteristic energy associated with its own electronic transition (SHINDO; OIKAWA, 2002). In this regard, while analyzing the silica gel EDS is expected to visualize a peak from the silicon atoms, at around the range of 1.740 keV, and another for the oxygen, at the range of 0,523 keV (NEWBURY; RITCHIE, 2012). However, the preparation for the sample of silica gel requires the addition of another material electrically conductive such as gold or silver. This addition may cause a peak characteristic of the element that must be neglected.

One of the limitations of the EDS analysis is the classification of elements such as hydrogen. Moreover, this technique can be used for quantitative intentions, but only if the atoms for this have a proton number equal or higher than the sodium (11 protons), if the sample has substances such as carbon or oxygen, the equipment is able to verify its presence but will not be capable to determine quantitative characteristics of the sample (NEWBURY; RITCHIE, 2012).

Furthermore, if the silica has not undergone proper treatment, is supposed to appear peaks for elements such as carbon, silicon, chlorine, bromine, and sulfur that are elements present on the organic compounds, in which the silica was used as stationary phase for the silica gel chromatography. Elements that are very common on organic molecules, such as carbon and oxygen can be detected by this technique, but the results from these atoms only have qualitative results and cannot be used as quantitative character.

2.4 Infrared Spectroscopy (IV)

Infrared spectroscopy analysis is a technique used to identify the functional groups of compounds with covalent bonds by absorbing infrared radiation, creating an infrared spectrum represented by a %T (transmittance) vs cm^{-1} (wavelength) graphic (PAVIA *et al.*, 2013; HAGE; CARR, 2012). Each molecule absorbs a certain frequency of infrared radiation that corresponds to its natural vibrational frequency, such as its stretching and deformation movements. Therefore, the energy absorbed is used to amplify these vibrational movements which occur in a quantized way. However, only bonds that have a non-zero dipole moment that vary with time or bonds that are not symmetric can be detected by this range of radiation (PAVIA *et al.*, 2013).

Because of that, each substance analyzed by this method will generate a unique spectrum showing in that way equivalence between known compounds with an unknown analyte. Thus, spectroscopy method provides qualitative evidence to identify the substance being analyzed. In that way, it can be used to compare the new silica with the purified one, showing if this last one has any impurities. Ideally, both should have the same bands and some intensity corresponding to silanol, siloxane groups and geminal silanol groups only (LOPES; FASCIO, 2004).

2.5 Thermogravimetry Analysis (TGA) – Differential Scanning Calorimetry (DSC)

Thermal analyses are techniques that examine sample properties as a function of temperature and time under specific environmental conditions. There are several thermal methods, but the focus of this article is on the thermogravimetric analysis (TGA) and the Differential Scanning Calorimetry (DSC) (FERREIRA; PEREIRA; NEVES, 2019; PEREIRA *et al.*, 2009). This process is utilized to determine characteristics such as decomposition, sublimation, oxidation, and dehydration of the samples. It records the mass loss or gain depending on the temperature and/or the time by varying the heat in the range of 25 to 1500 °C at a rate of 10 °C per minute (LAZZARA; DONATO; MILIOTO, 2010). The equipment consists of a high sensible thermal scale, a temperature sensor, a recorder system, and a gas source so the circumstances are the same for every compound tested (FERREIRA; PEREIRA; NEVES, 2019).

These analyses generate graphics with mass and temperature in the axis by forming different peaks depending on the loss or gain of mass for each sample or with more than one result to easily compare the compounds. To facilitate even more the interpretation of the graphics, it is used Derivative Thermogravimetry which is, as the name says, the derivative of the thermogravimetric curve. Therefore, this technique increases the resolution of the curve by showing more precisely the areas where the sample has constant rate of weight changing and making it possible to observe this variation by the heights of the peaks. Although, it cannot be used when there is a small rate because that would form a line and, by definition, the derivative of a line is null (FERREIRA; PEREIRA; NEVES, 2019; PEREIRA *et al.*, 2009).

Besides Thermogravimetry, another important thermal analysis is Differential Scanning Calorimetry (DSC). This method is used to find out if the sample has another component besides the ones that form the desired product by showing its composition and, with that, shows its purity (MOREIRA *et al.*, 2010). It works by examining the sample enthalpy during a controlled variation of temperature comparing it to the enthalpy of a reference compound, which means that the technique is different from the one explained before because it measures the alteration of energy of the sample tested (FERREIRA; PEREIRA; NEVES, 2019; GILL; MOGHADAM; RANJBAR, 2010). The temperature range of this machine goes from 40 to 500 ºC and it changes at a rate of 10 ºC per minute such as TGA (WANG *et al.*, 2009).

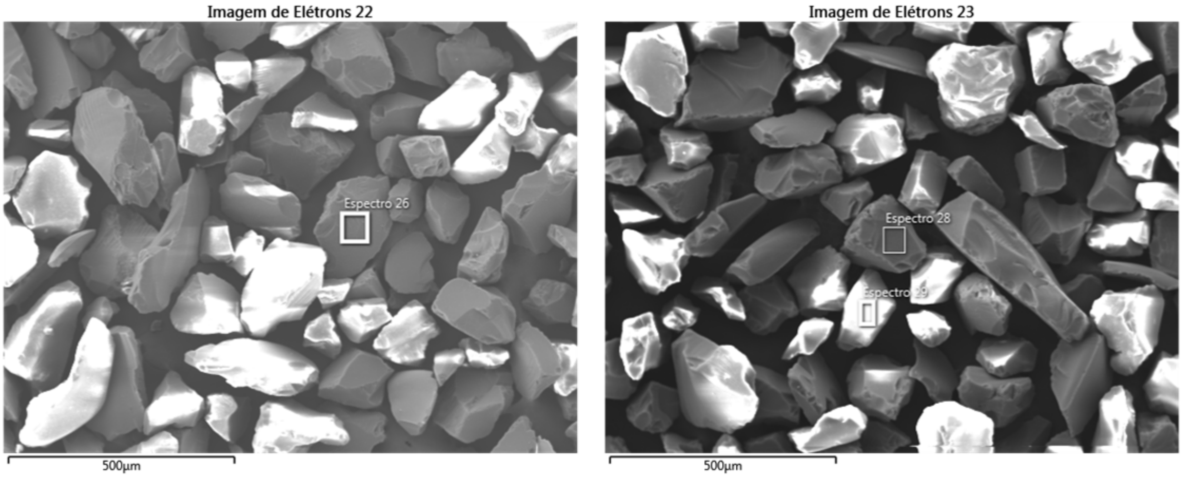
Differential Scanning Calorimetry can be done in two different ways called Power-compensated DSC and heat flux DSC. In the first technique, the sample and the reference are placed in separate compartments, where the temperature varies at the same rate for both. Thus, the variation of energy in each compound will not affect the other because the machine will compensate for it, so its sensors calculate the amount of energy due to this compensation. In the second method, both compounds are tested in the same environment. Therefore, the variation of energy of one of the samples affects the environment and the other sample, so its sensors measure the heat flux (FERREIRA; PEREIRA; NEVES, 2019).

The equipment used in this study is a power-compensated DSC, which generates thermograms that reflect the exothermic or endothermic behavior of the sample. If the substance releases heat and energy, the graphic will show a peak pointing to the axle of the temperature or the time, but if it absorbs energy and heat the peak will point in the opposite way, where the heat flux is higher (BERNAL *et al.*, 2002). Silicon dioxide is an endothermic compound, which means that the expected graphic of the commercial and treated silica has a peak steering to the axle.

3 RESULTS AND DISCUSSION

During purification, the loss of small particles could occur, resulting in a change in silica size (denominated mesh). Figure 2 shows the SEM images for the samples, the pattern from Aldrich® and the treated silica GC1039B. Upon analysis of the pictures taken by the equipment, it was not possible to discern any significant differences between them.

Figure 2 – SEM images of silica gel samples, Aldrich® (left), GC1039B(right). (Original magnification 100x)

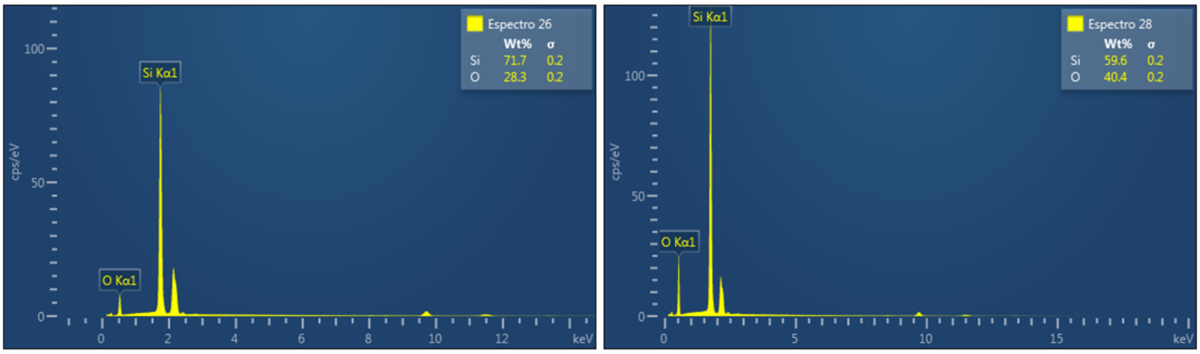


Source: Developed by the authors.

Figure 3 shows the EDS analysis. It is possible to visualize the peaks from Silicon atoms, in the range of 1.70 keV (Kα1, representing the most probable electronic transitions between the electronic shells), and the peaks from oxygen atoms at 0.52 keV (also Kα1). Both the elements were indicated by the equipment and are befitting with the literature (NEWBURY; RITCHIE, 2012). Moreover, if the treatment for the silica gel was not effective it was expected to appear peaks from other elements, such as chlorine (Cl), at some point around 2.6 keV, and carbon atoms, at the range of 0.2774 keV. Besides, these atoms are present in organic molecules in which the silica gel was used as a stationary during chromatography purification.

The peak in 2.12 keV that is not identified on the image is a characteristic peak from gold atoms (NEWBURY; RITCHIE, 2012). Because silica is not electrically conductive, it was necessary to use a small amount of gold so the analysis could be realized.

Figure 3 – EDS analysis of silica gel samples, Aldrich® (left), GC1039B (right)

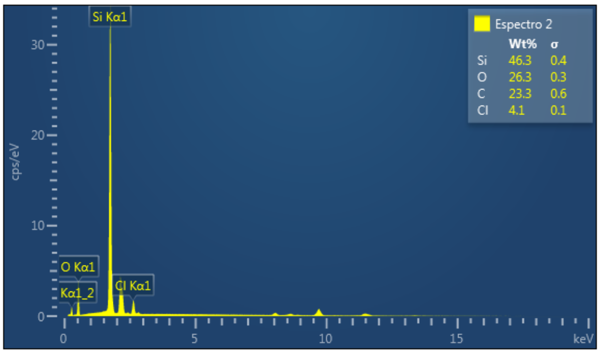


Source: Developed by the authors.

The EDS for the silica pre-treatment is exemplified in the Figure 4, it is possible to see other peaks from different elements, suggesting that this material was contaminated with another compounds, after its utilization in silica gel chromatography. The equipment showed peaks of substances such as chlorine 2.62 keV and carbon 0.2774 keV, these are elements present on the organic molecules that have been purified, but may be present in the silica, after its use, as residue from the process (GRIEKEN; MARKOWICZ, 2006).

Besides the nitrogen atoms being part of the purification molecules, as can be observed in the IV spectrum of Figure 4, it appears in lower quantities compared to other atoms, such as chlorine and carbon. This fact results in difficulty for the equipment to demonstrate the presence of nitrogen atoms due to its lower concentration.

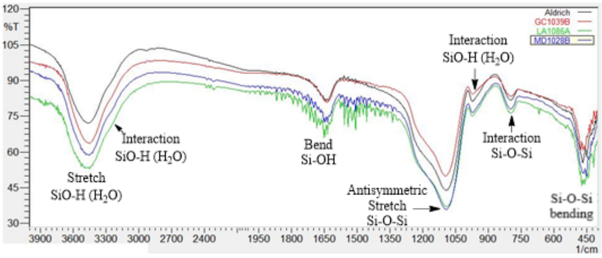
Figure 4 – EDS analysis of silica gel sample before the treatment and after it has been used as stationary phase



Source: Developed by the authors.

Figure 5 shows the four spectra obtained for the silica samples, including a silica from a new open flash from Aldrich® and the samples from the treated silica that were done by three different researchers in different days and following the same methodology.

Figure 5 – Spectra of the silica samples, in red the sample from Aldrich® and the others from the present study after treatment

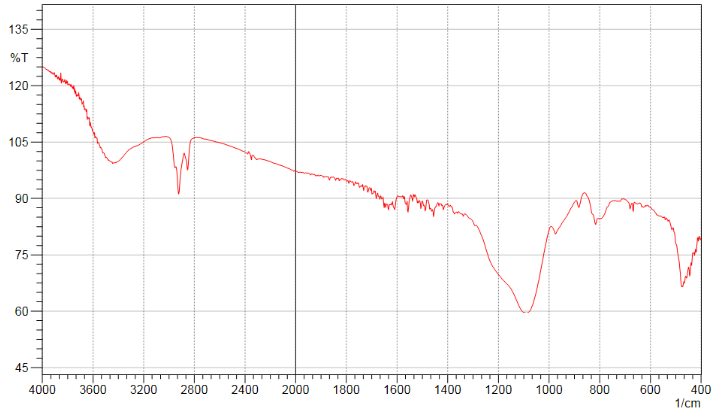


Source: Developed by the authors.

Theoretically, the characteristic bands expected to observe in a silica spectrum are Si-O-Si antisymmetric stretching around 1111 cm^{-1} region, Si-O-Si symmetric stretching around 800 cm^{-1} region and Si-O-Si bending at 468 cm^{-1} region. If water is present in the sample, it is also expected OH stretching around 3437 cm^{-1} region, OH bending around 1632 cm^{-1} region, Si-O-H deformation around 3238 cm^{-1} region, confirmed by a signal around 970 cm^{-1} which represents the silanol groups (MUSIĆ; FILIPOVIĆ-VINCEKOVIĆ; SEKOVANIĆ, 2002).

In case the impure silica, after the treatment, it was expected to appear peaks that show amine and halogen-based compounds, because of its previous utilization in silica gel chromatography during another research made in the Organic Laboratory. As an example of this, Figure 6 shows the IV spectrum for the silica gel before the treatment. It is possible to see the appearance of some characteristic carbon peaks. First peak, around 3600-3500, correspond to –OH stretching of silanol or presence of water, followed by the aromatic stretch in the range of 3100-3000 cm^{-1}, C-N ring stretching in the range of 1600 to 1430 cm^{-1} and the aryl chloride stretch in the range 1160 to 1020 cm^{-1}, probably overlapped by the Si-O-Si asymmetric stretching (SILVERSTEIN *et al.*, 2005). These peaks are not found in silica gel after the treatment which suggests that the exhaustive oxidation process was effective on removing the organic impurities being effective as a mean to remove organic compounds.

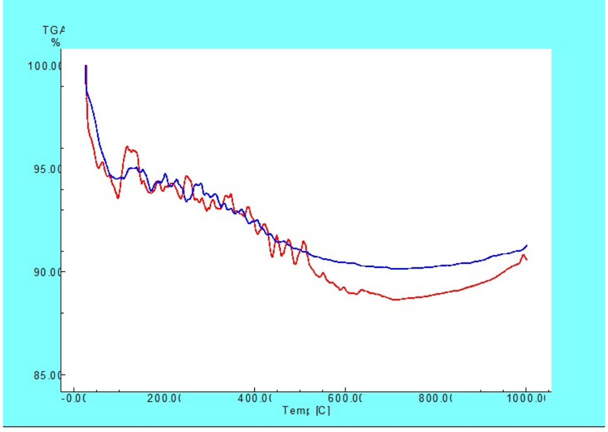
Figure 6 – Spectrum of the silica samples before treatment



Source: Developed by the authors.

Thermogravimetry analysis shows the variation of the compound mass, while it is under a constant rise of temperature. With an atmosphere consisting of nitrogen gas (N_2), and a heating rate of 10°C min^{-1} the results of the test are shown in the following figures. Figure 7 represents the total mass variation between the samples, the blue curve represents the silica gel used as a pattern, while the red curve represents the treated silica.

Figure 7 – TGA for silica gel Aldrich® (blue) and GC1039B (red)



Source: Developed by the authors.

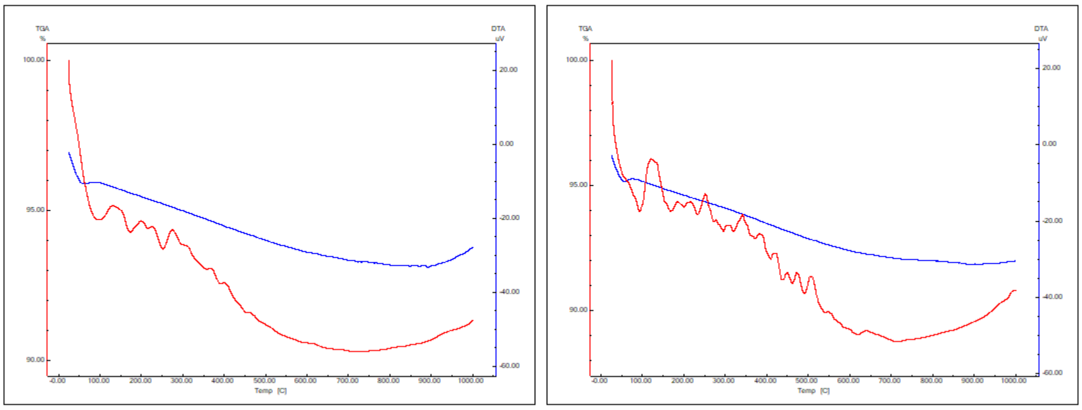
As can be seen in Figure 7, in the temperature range between 30°C and 100°C, the pattern lost 4.25% of mass while the other samples lost an average of 4.32% of mass, this mass loss is referent to residual water and moisture on the samples. In addition, in the second region, between 100-600°C, the mass loss is caused probably by water coming from the silanol groups that are present in the surface of the material. Upon comparison of the mass loss values, both the standard and the GC1032B sample (red curve in Figure 5) exhibited equivalent mass losses, approximately 4.2%, indicating similar thermal stability under the tested conditions. The flowchart in Figure 8 shows the mass loss of the TGA process.

Figure 8 – Flowchart of the mass loss of TGA

Source: Developed by the authors.

Figure 9 shows the same TGA in Figure 7, but it also displays the DTA results for the standard and the sample obtained under identical heating conditions. This figure shows that, for all the samples, the thermal behavior is very similar.

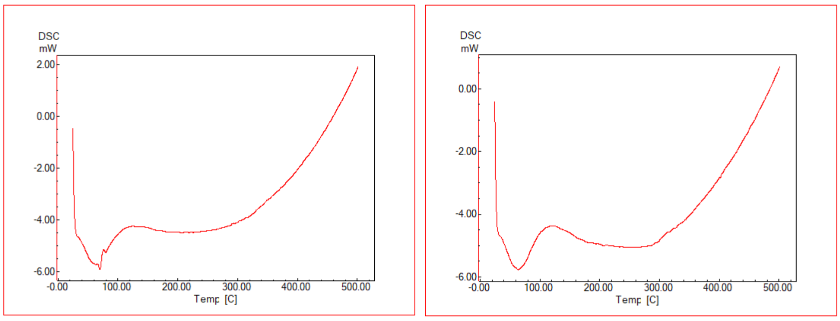
Figure 9 – TGA and DTA for silica gel Aldrich® (left) and GC1039B (right)



Source: Developed by the authors.

Regarding the DSC, the behavior of all the silica samples follows the same tendency of the thermogravimetric analysis with no alterations. If the silica was contaminated with organic compounds, major differences between both were expected. In Figure 10, DSC results demonstrate the energy absorption, which means that the reaction is endothermic. This is possible to be seen because the graphic shows that the environment is losing energy to the sample (the graphic line is below 0 mW). The silanol groups in the silica molecule break bonds with silicon and form chemical water, as evidenced by the bands observed in the infrared spectrum. Besides that, there is also physical water from the air humidity in the samples. When the test reaches the temperature of 30°C, this water starts to evaporate until it gets to 100°C, that is the reason why it is possible to notice a higher absorption of energy in this range (FERREIRA; PEREIRA; NEVES, 2019). Within the temperature range of 160 to 300°C, it becomes evident that the substance exhibits increased energy absorption due to undergoing a fusion event followed by subsequent recrystallization (ALVES, 2007).

Figure 10 – DSC Analysis for silica gel Aldrich® (left) and GC1039B (right)



Source: Developed by the authors.

During the experimental procedure, after the addition of sodium oxalate, two different results were observed. When the process was done continuously, it was observed that the solution turned pinkish, and the silica turned whitish. The pink solution is explained by the formation of manganese with an oxidation state of +2 (Mn^{+2}), by the reduction half-reaction shown in Reaction 4:

$$\mathrm{MnO}^-_{4(aq)} + 8\,\mathrm{H_3O}^+_{(aq)} + 5\,e^- \rightarrow \mathrm{Mn}^{2+}_{(aq)} + 12\,\mathrm{H_2O}_{(l)} \tag{4}$$

However, during our attempt to quantify the process, it was observed in some experiments that both the solution and the silica turned dark brown. The group's proposal is that it occurs due to the system being less acid than it should be to reduce the manganese that was in higher oxidation states to +2. It is well known that potassium permanganate in neutral conditions produces manganese dioxide as shown in Reaction 5.

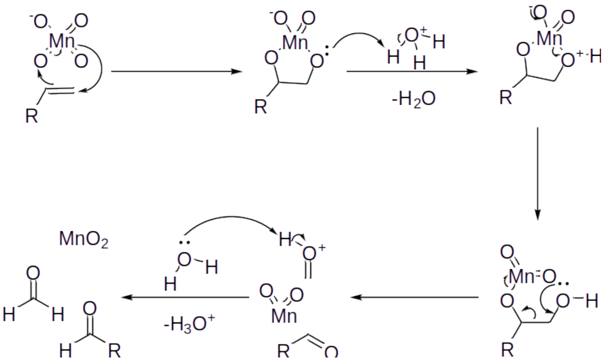
$$\mathrm{MnO}^-_{4(aq)} + 2\,\mathrm{H_2O}_{(aq)} + 3\,e^- \rightarrow \mathrm{MnO}_{2(s)} + 4\,\mathrm{OH}^-_{(aq)} \tag{5}$$

Additionally, because of its instability, it can react with light and the components of the air, decomposing to manganese dioxide as shown in Reaction 6:

$$4\,\mathrm{MnO}^-_{4(aq)} + 4\,\mathrm{H_3O}^+_{(aq)} \rightarrow 3\,\mathrm{O}_{2(g)} + 4\,\mathrm{MnO}_{2(s)} + 6\,\mathrm{H_2O}_{(l)} \tag{6}$$

Moreover, the production of manganese dioxide can be explained by the mechanisms proposed by the group, as shown in Scheme 1. Mechanism proposal of oxidative reaction involving KMnO4 and organic compounds in acidic conditions.

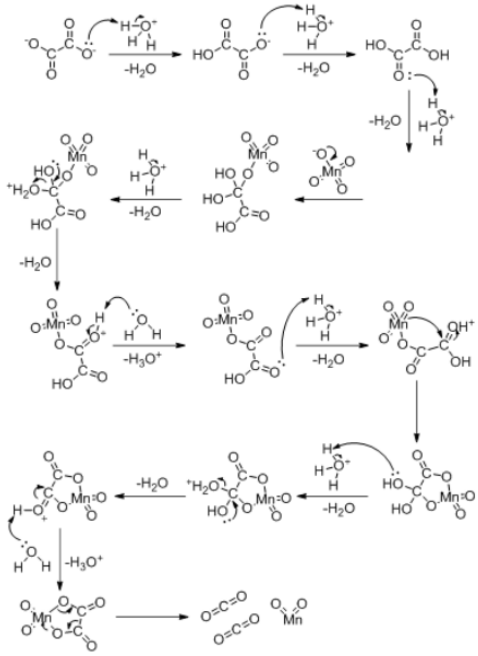
Scheme 1 - Mechanism of manganese dioxide formation



Source: Developed by the authors.

Mechanism proposal of the reaction between sodium oxalate and potassium permanganate in acid conditions is shown in Scheme 2.

Scheme 2 - Mechanism of MnO_2 formation in acid conditions



Source: Developed by the authors.

Due to all these explanations, plus the fact that is observed the generation of a brown solid, the contamination is assumed to be manganese dioxide (MnO_2).

As an alternative to solve this problem, the oxidative process can be redone by the addition of sulfuric acid and potassium permanganate in small quantities, until the pinkish coloration is achieved, followed by the addition of sodium oxalate and more sulfuric acid. Increasing the tendency of the formation of Mn^{2+} as it can be showed in Scheme 2. Furthermore, to achieve better results, the entire process must be done continually and as fast as possible.

4 CONCLUSION

Silica purification involving physical and chemical processes demonstrates to be an effective and low-cost procedure. Several methods were used to analyze purity of the resulting material. Industrial application to provide and purify larger amounts of used silica is a feasible way.

Acidic oxidative method using potassium permanganate can produce several products, thus the proposed mechanisms were used to explain some generated compounds. Infrared spectroscopy was used to shown silica structure as well as presence of impurities. SEM, EDS, TGA and DSC also provided important information about structure and composition of silica to prove that the proposed treatment works.

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