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Effect of thermal and argon plasma treatment in SiO_2 spheres, assessing the effectiveness in the elimination of organic waste

Efecto del tratamiento térmico y de plasma de argón en esferas SiO_2, evaluando la efectividad en la eliminación de residuos orgánicos

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Abstract

Cetyltrimethylammonium bromide (CTAB), is a cationic surfactant used in synthesis of silica oxide spheres (SiO_2), which can be used in biomedical applications, however, CTAB is cytotoxic and residues can be found within the SiO_2 pores, therefore, the removal of CTAB, is crucial. In the present work, the preparation and purification of SiO_2 is described. The effect of heat treatment against argon plasma treatment on SiO_2 spheres and their efficiency in removing CTAB was analyzed. The plasma treatment was performed using argon, at 50, 100, 150 and 200 W of power, for 1 h, it was also performed at 200 W for 1.5 h. The techniques; DLS, FTIR-ATR, SEM, BET, were used for characterization, in addition to hemolysis studies. The results showed a decrease in surfactant at powers of 150 and 200 W and 1 h. The plasma treatment at 200 W and 1.5 h of treatment, according to the FTIR-ATR, caused a total removal of the surfactant and a 16% increase in the surface area according to the BET analysis, the plasma treatment turned out not to be hemolytic.

Keywords: Biomedical applications, plasma Treatment, silica oxide; heat treatment.

Resumen

El bromuro de cetiltrimetilamonio (CTAB) es un tensioactivo catiónico utilizado en la síntesis de esferas de óxido de sílice (SiO_2), que se puede utilizar en aplicaciones biomédicas, sin embargo, el CTAB es citotóxico y se pueden encontrar residuos dentro de los poros de SiO_2, por lo tanto, la eliminación de CTAB, Es crucial. En el presente trabajo, se describe la preparación y purificación de SiO_2. Se analizó el efecto del tratamiento térmico contra el tratamiento con plasma de argón en las esferas de SiO_2 y su eficacia en la eliminación de CTAB. El tratamiento con plasma se realizó con argón, a 50, 100, 150 y 200 W de potencia, durante 1 h, también se realizó a 200 W durante 1,5 h. Las técnicas; DLS, FTIR-ATR, SEM, BET, se utilizaron para la caracterización, además de los estudios de hemólisis. Los resultados mostraron una disminución en el tensioactivo a potencias de 150 y 200 W y 1 h. El tratamiento con plasma a 200 W y 1,5 h de tratamiento, de acuerdo con el FTIR-ATR, provocó una eliminación total del tensioactivo y un aumento del 16% en el área de superficie según el análisis BET, el tratamiento con plasma resultó no ser hemolítico.

Palabras clave: Aplicaciones biomédicas, tratamiento con plasma, óxido de silicio, tratamiento térmico.

1 Introduction

In recent years, porous silica nanoparticles (SiO_2) have attracted great attention in various applications, due to their intrinsic properties (Oliva *et al*., 2018; Whitaker, 2019). These particles have a unique structure, with mesoporous sizes of 2-50 nm. In addition, these nanoparticles have a large specific surface area that varies between 500 to 1500 cm^2/g and pore volume of 1 cm^3/g, which is regular and modifiable, they also contain a high density of silanol groups (Si-OH) (Wang *et al*., 2015).

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SiO_2 particles are a stable, non-toxic, this is a platform for biomedical applications such as theranostics and controlled drug delivery systems (Hudson *et al*., 2015; López-Alemany *et al*., 2002; Tang *et al*., 2006; Rahman *et al*., 2012). On the other hand, studies have been conducted on the relationship of shape, size and texture with its efficiency in this type of applications, which it has been necessary to look for new synthesis methods to obtain SiO_2 particles adapted to the needs sought by the user. In the case of methods to produce silica particles specifically for biomedical applications, new methods have been developed in order to produce unique silica particles, synthesized from a precursor solution (Rahman *et al*., 2012; Meier *et al*., 2018; Schachter *et al*., 2013), however, the use of certain reagents during their synthesis can limit the biomedical applications of these particles. A clear example is the use of surfactants, such as CTAB (hexadecyltrimethylammonium bromide), since this reagent is particularly problematic for biological applications due to its cytotoxicity (Schachter *et al*., 2013; Wawang *et al*., 2010; Alkilany *et al*., 2009; Zaho *et al*., 2016). CTAB promotes the formation of porous SiO_2 in the size range between 50 to 250 nm (Gao *et al*., 2018; Martínez *et al*., 2016; Palaniappan *et al*., 2004), essential characteristics for drugs administration. Besides, there are some methods like heat or plasma treatment that will help to remove chemical impurities such as CTAB from SiO_2 particles (Palaniappan,*et al*., 2004).

Heat treatment is the conventional method reported for CTAB removing (He et al, 2019; Lei et al, 2017). For instance, Vidonish et al, Santos-Beltran et al, have reported that is effective in the removal of organic compounds like CTAB in compounds with silica (Vidonish *et al*., 2016; Santos-Beltran *et al*., 2018) however, some studies have shown that thermal treatment could change the particle structure and affect its final function (Lei *et al*., 2017). On the other hand, surface modification with plasma could be used as an emergent technology, since it has the ability thus achieving the total or partial elimination of unwanted substances, such as CTAB at short treatment times (Reyna-Martínez *et al*., 2018; Centre *et al*., 2013).

The cold or non-thermal plasmas (NTAP) are generated by the application of an electric or electromagnetic field to a gas, in this case Argon (Ar). The field energy, causes the free electrons to accelerate and ionizes the gas atoms and molecules, which release more free electrons that in turn provoke new ionizations. Consequently, the plasma is constituted basically by molecules and atoms in an excited state, positive and negative ions, free radicals, electrons, UV radiation and reactive oxygen and nitrogen species, such as ozone, superoxide, hydroxyl radicals, singlet oxygen, atomic oxygen, nitric oxide or nitrogen dioxide to mention an example.

The aim of this research is to evaluate the effect of thermal treatment and plasma treatment on SiO_2 particles, and the effectiveness in the removal of CTAB and their hemolytic behavior.

2 Methodology

2.1 *Synthesis of silica oxide*

The synthesis of silica was carried out by the standard sol-gel method (Meier *et al*., 2018; Zno *et al*., 2019). Briefly, under vigorous stirring, 0.8 g of CTAB was dissolved in 100 mL of water and 30 mL of anhydrous ethanol. Once homogenized, 0.8 mL of ammonium hydroxide and 20 mL of ethyl ether were added to the solution and then 2.5 mL of the TEOS precursor was added dropwise, leaving it to react during 4 h. The obtained silica was washed and centrifuged three times with a mixture of 50% water and 50% anhydrous ethanol and allowed to dry for 12 h at 100 °C.

2.2 *Plasma treatment of SiO_2 particles*

The plasma treatment was performed in an armed team in our laboratory, which consists of in a radiofrequency, rotary reactor (Soria-Arguello *et al*., 2018) at 13.56 MHz, using argon (Ar) gas. With the objective of erosion, the nanoparticles of SiO_2 and at the same time eliminate the CTAB, that you could be anchored on the surface. The treatment was carried out at 50, 100,150 and 200 W of input plasma power, at a pressure of 4.5 x 10^{-1} mbar for 1 h and a treatment at 200 W for 1.5 h was also carried out.

2.3 *Heat treatment of SiO_2 particles*

The heat treatment was carried out in a Thermolyne 46100 High Temperature Chamber Furnace stove at 450 and 600 °C respectively for 6 h at a heating rate of 1 °C per minute.

2.4 *Hemolysis test of SiO_2 particles*

Blood from healthy human volunteers was obtained with syringes with EDTA and placed into sterile

polypropylene tubes according to the Ethics Research Committee from University of Coahuila. A written informed consent was obtained from each subject prior to participation in the study. The blood was collected in EDTA-tubes and centrifuged at 3000 rpm for 4 minutes at 4 °C. The pellet obtained was washed three times with cold Alsever solution (0.116 M dextrose, 0.071 M sodium chloride, citrate sodium 0.027 M and citric acid 0.002 M). The supernatant was diluted 1:99 with the Alsever solution. Then, 150 μL of this suspension were taken for the experiments. This suspension of red blood cells was always prepared fresh and was used within 24 h after collection. SiO_2 samples with and without treatment were prepared in concentrations of 1, 2 and 5 mg/mL Subsequently, the tubes were gently mixed on a rotary shaker and incubated at 36.5 °C in a shaking water bath for 1 h. The Alsever solution and the deionized water were used as negative and positive controls, respectively. The samples were centrifuged at 3000 rpm for 4 minutes and the free hemoglobin in the supernatant was measured spectrophotometrically by UV at 415 nm (Sinergy model HTX). The percentage of hemolysis was calculated using the following equation (Eq 1):

$$\%Hemolysis = \frac{abs\ sample - abs\ negative\ control}{abs\ positive\ control - abs\ negativecontrol} \times 100 \quad (1)$$

Note: $abs = absorbance$.

The tests were interpreted considering the recommendations of ASTM F 756 00, which consider a hemolytic activity above 5%, between 2% and 5% slightly hemolytic and below 2% non-hemolytic (ASTM, 2004). The hemolysis assays were performed in triplicate and the data are representative of three independent experiments.

The times proposed by various authors in studies related to biomaterial hemolytic tests (Acuña-gutiérrez *et al*., 2017; Macías-martínez *et al*., 2016; Muzquiz-Ramos *et al*., 2012), (Henkelman *et al*., 2009)where they indicate, that the hemolysis result, is given in the first hours of testing, so long periods of time are not necessary, since it is obtained as a result few hemolytic differences according to the incubation times, as long as the parameters are controlled as temperature (37 ºC).

2.5 *Characterization of SiO_2 particles*

2.5.1 *DLS (Dynamic light Scattering)*

A DLS system was used to obtain the size particle distribution, the analyzer model Nanotrack Wave II was used with a 180° backscatter arrangement. Subsequently, the counting of the average particle diameter size was carried out using the software ImageJ 1.47 v. The samples were dispersed in distilled water for their analyses.

2.5.2 *FTIR-ATR*

The FTIR-ATR spectra of SiO_2 were performed on an equipment model Thermo Scientific Nicolet iS10 in a range of 600 to 4000 cm^{-1} with 100 scans and a resolution of 0.4 cm^{-1}. The samples in powder were analyzed without any additional treatment.

2.5.3 *BET technique*

The Brunauer-Emmet-Teller (BET) specific surface area and Barrett-Joyner-Halenda (BJH) pore volume of the SiO_2 samples were determined from nitrogen adsorption-desorption isotherms. The isotherms were obtained using an equipment model Quantachrome AS1Win.

2.5.4 *SEM*

The morphological characterization of the silica before and after the treatments, was carried out in a scanning electron microscope of field emission SEM brand FESEM, Hitachi SU8010, operated at a voltage of 1 to 10 kV. The samples were coated with gold nanoparticles to facilitate electrical conductivity prior to analysis.

3 Materials

Reagents used for silica synthesis were purchased from Aldrich and used without additional treatment; tetraethyl orthosilicate $Si(OC_2H_5)_4$ (TEOS, 98%), cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$) (CTAB, 99%), sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$) and ammonium hydroxide (NH_4OH). Anhydrous ethanol with 99% purity was used (Jalmek Scientific, México).

4 Results and discussion

4.1 Dynamic light scattering (DLS)

The analysis of the size of hydrodynamic diameter obtained in the synthesis of the particles of silicon oxide was studied by means of DLS. The average particle size obtained was 172 nm varying between 150 and 240 nm, observing a polydispersity of ± 69 nm.

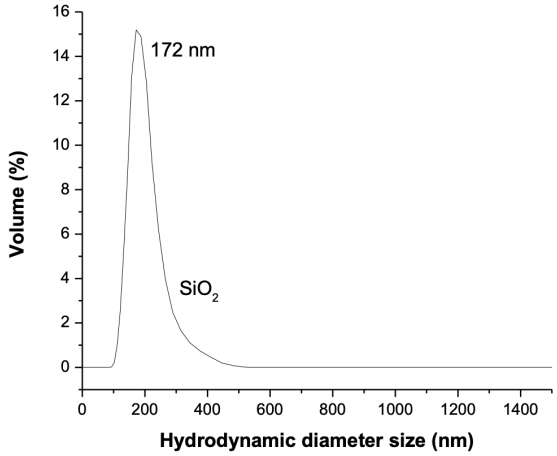

Fig. 1. Size distribution of SiO_2, obtained by DLS analysis.

4.2 FTIR-ATR Spectroscopy

The effect of the heat treatment and the argon plasma treatment of SiO_2 spheres and its potential application in the elimination of CTAB was evaluated. A FTIR-ATR Spectroscopy study was carried out in order to determine the changes in the chemical structure of the SiO_2 spheres after the two different types of treatment. In Figure 2, the FTIR-ATR spectra of the thermally treated SiO_2 particles are shown. In Figure 2a the presence of the characteristic vibrations of SiO_2 is observed, in 567 cm^{-1} pertaining to the flexion of the Si-O bond, the band at 962 cm^{-1} is related to the stretching of O-Si-O bonds, the bands located at 962 and 1049 cm^{-1} are characteristics of Si-O Si bonds. In addition, the characteristic signals of the organic residues derived from the use of CTAB surfactant (2922, 2851 and 1478 cm^{-1}) can be observed in the spectrum. Figure 2b show an amplification of the region where the characteristic bands of the CTAB are located, the bands attributed to the residues of the CTAB (2922, 2851 and 1478 cm^{-1}) were eliminated during the treatment at 600 °C.

In Figure 3 the FTIR-ATR spectra of the SiO_2 particles pristine and treated by plasma are shown. Figures 3a and 3b show SiO_2 particles after plasma treatment at energies of 50, 100, 150 and 200 W respectively. Besides, it was observed that as the plasma potency increases, the absorbance of the bands attributed to methyl and ethyl groups gradually decreases. This indicates that organic waste derived from the use of CTAB surfactant (2922, 2851 and 1478 cm^{-1}) is decreased.

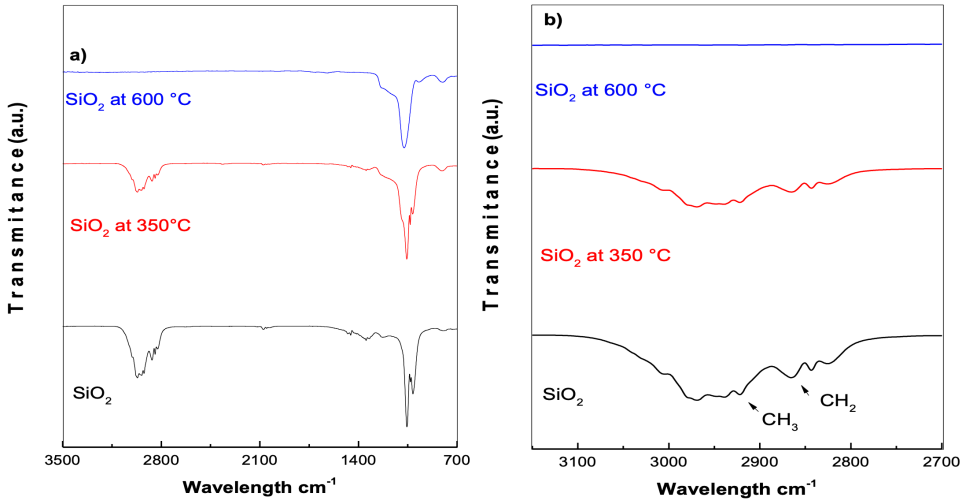

Fig. 2. FTIR-ATR spectra of thermal treatments of SiO_2 particles.

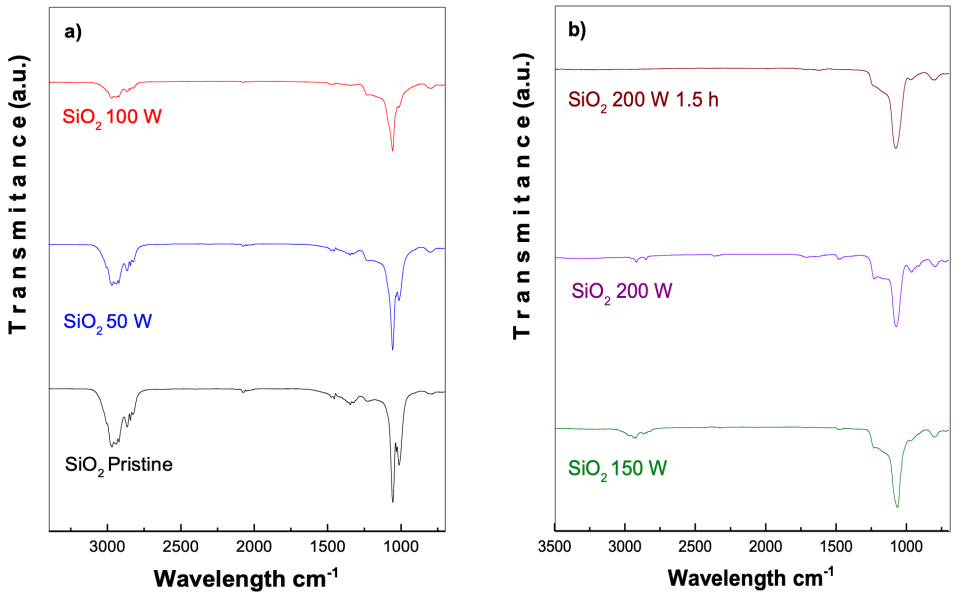

Fig. 3. FTIR-ATR spectra of SiO_2 particles.

The results in the Figure 3b indicated that the treatment at 200 W for 1.5 h eliminated the CTAB bands. In this way, the results obtained by Infrared Spectroscopy demonstrated that both methods are efficient in the elimination of the surfactant. However, the technique of modification by plasma has the advantage that it is a faster technique and with a lower energy expenditure than the thermal treatment.

4.3 Scanning electron microscopy (SEM)

Figure 4 shows the micrographs of pristine SiO_2 and SiO_2 thermally treated and modified with plasma. Figure 4a shows the micrograph of pristine SiO_2. It shows that SiO_2 has a spherical morphology. The micrograph of Figure 4b indicate that SiO_2 spheres collapse and agglomerate, completely losing their spherical morphology and the nanometric size, due to the thermal treatment of 600 °C during 6 h at 1 °C/min. Figure 4c shows the SEM micrograph of SiO_2 particles with plasma treatment at 200 W for 1.5 h. Also, it was observed that although the SiO_2 particles had agglomerated, they still presented a spherical morphology, with surface roughness that can be observed at a glance. From the micrographs obtained by SEM it can be observed that the plasma treatment of argon is a less aggressive treatment than the heating treatment, since the particles retained their original morphology.

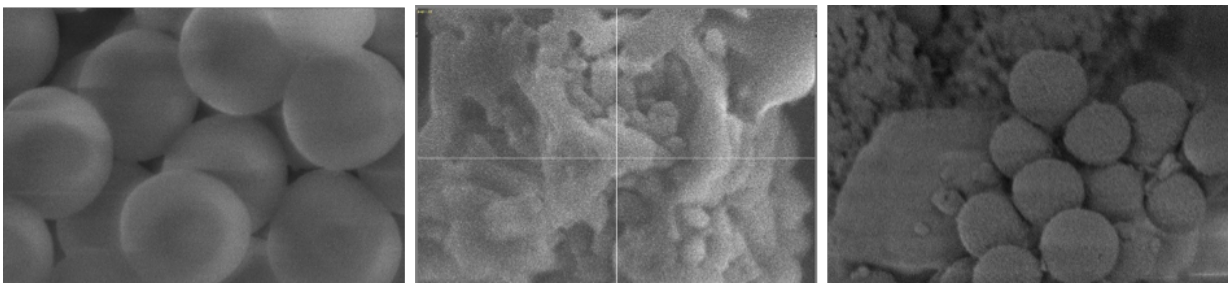

Fig. 4. SEM micrographs from left to right, a) Pristine SiO_2, b) SiO_2 treated at 600 °C, c) SiO_2 treated by plasma at 200 W.

4.4 BET technique

In order to eliminate the surfactant used as a template in the synthesis of spherical silica particles, the thermal treatments (450 °C and 600 °C) and plasma (150 W and 200 W) were used. Figure 5 and Table 1 show the results obtained by the BET technique. Pristine SiO_2 particles and the SiO_2 sample calcined at 450 °C present surface area values of 4.43 cm^2/g and 4.61 cm^2/g, respectively; both samples show an adsorption-desorption isotherm type 4 that corresponds to mesoporous materials (Lei *et al*., 2017; Wang *et al*., 2018). Also, both samples have a pore volume of 0.016 cm^3/g and a pore diameter size of 36 nm. On the other hand, the sample treated at 600 °C has a surface area value of 76.56 cm^2/g and its pore size value is 3.62 nm, which indicates that it is within the range of mesopores (Wang *et al*., 2018) also is observed that this sample has a characteristic isotherm of type I. Regarding to analysis of the adsorption-desorption isotherms of the SiO_2 samples treated with plasma at 150 W and 200 W, it was found that both samples have similar values of specific surface area (see Table 1) but their pore volume and pore size values are different; the isotherms of adsorption-desorption for these samples is type III, which suggests the presence of macroporous. The sample of SiO_2 that was treated at 200 W has a specific surface area value of 27.25 cm^2/g, a pore volume of 0.508 m3/g and a pore diameter of 784 Å (See Table 1); this specific surface area value is 6 times higher than of the SiO_2 pristine. It is important to mention that the treatment of the SiO_2 particles at 600 °C allows to get SiO_2 particles with the higher specific surface area value (76.56 cm^2/g), but the pore volume and pore size values are lower than of the silica sample treated with plasma at 200 W. This is due to the SiO_2 particles coalesce at 600 °C, as can be seen in Figure 4, forming non-spherical particle agglomerates. This means that the thermal treatment given to the SiO_2 particles at 600 °C does not make them suitable for biomedical applications, while the SiO_2 particles modified by plasma retained their quasi-spherical geometric shape that is suitable for this type of applications.

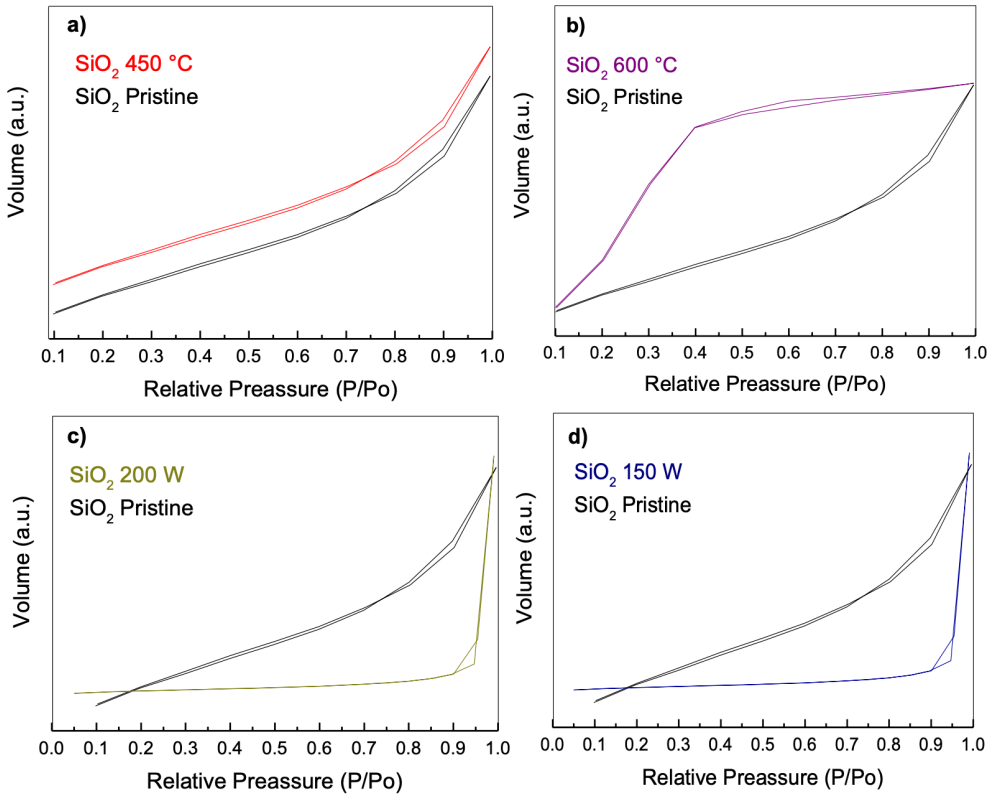

Fig. 5. Nitrogen adsorption-desorption isotherms of a) Pristine SiO_2 vs SiO_2 450 °C, b) Pristine SiO_2 vs SiO_2 600 °C, c) Pristine SiO_2 vs SiO_2 150 W, d) Pristine SiO_2 vs SiO_2 200 W.

Table 1. Results obtained by BET.

Sample	BET area (m^2/g)	Pore volume (cm^3/g)	Pore Diameter (nm)
SiO_2	4.43	0.016	36.0
SiO_2 450 °C	4.61	0.016	36.0
SiO_2 600 °C	76.56	0.095	36.2
SiO_2 150 W	26.04	0.435	66.8
SiO_2 200 W	27.25	0.508	78.4

4.5 Hemolysis assay

The interaction of SiO_2 particles with the blood components can lead to the lysis of human erythrocytes. For this reason, the effects of SiO_2 particles in the blood were evaluated with hemolysis assays. The results indicated that pristine SiO_2 and the sample treated at 450 °C were hemolytic at the concentration of 5 mg/mL while SiO_2 samples treated at 600 °C were hemolytic at the concentrations of 2 and 5 mg/mL, this effect was probably caused by the deformation of the structure of the SiO_2 particles as a result of the heat treatment, on the other hand, the samples treated with plasma at the different plasma input powers have no hemolytic effects in any of the concentrations analyzed (Fig. 6 and 7). Several authors have evaluated the basic ability of porous silica nanoparticles as drug carriers, obtaining favorable results in terms of hemolysis tests from nonhemolytic silica particles (Yingada *et al.*, 2019), and it has even been reported that the treatments with plasma treatment could suggest a protection of SiO_2 particles with respect to hemolytic effects (Madhura *et al.*, 2013), suggesting the potential use of plasma to design new controlled release systems.

4.6 Erosion mechanism in SiO_2

Based on the results obtained, in this research work, the erosion mechanism is proposed and, consequently, the elimination of CTAB, through plasma treatment, see figure 7. The mechanism of plasma erosion involves the removal of chemical groups to large sections of a given substrate. Erosion occurs when the reactive species of argon plasma (neutral argon atoms, energized argon atoms, free electrons and UV photons) impact on the surface of the CTAB breaking the chemical bonds that compose it, this is inferred since the free electrons in the plasma they have 20 eV of energy (Misra *et al.*, 2016) and UV photons with 3.2 eV (Bohorquez, 2007) so the plasma is capable of breaking common bonds in organic compounds (C-C, C-N, C-H) since specifically in the case of CTAB these links should have link energies between 3.0 and 4.3 eV (Ebewele, 2000). The aforementioned is inferred from the cited literature, however, information on the specific mechanism of CTAB degradation by Argon plasma action was not found in the specialized literature.

Unlike the plasma treatment, the thermal treatment consists in the degradation of the CTAB, as a result of exposing the SiO_2 nanoparticles, at high temperatures.

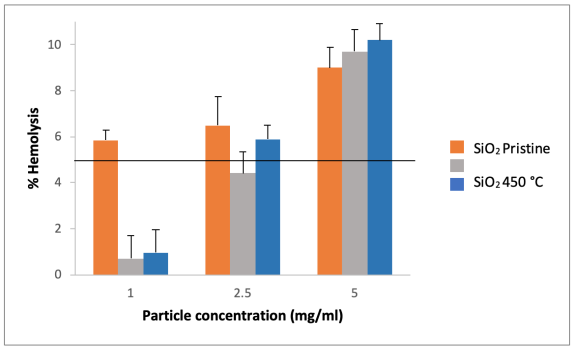

Fig. 6. Graph of results of hemolytic tests of pristine SiO_2 and SiO_2 exposed to thermal treatment.

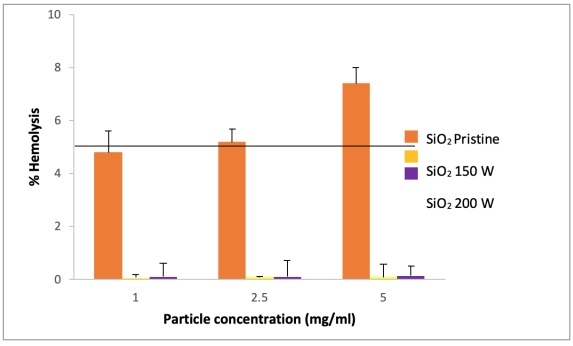

Fig. 7. Graph of results of hemolytic tests of pristine SiO2 and plasma treated particles.

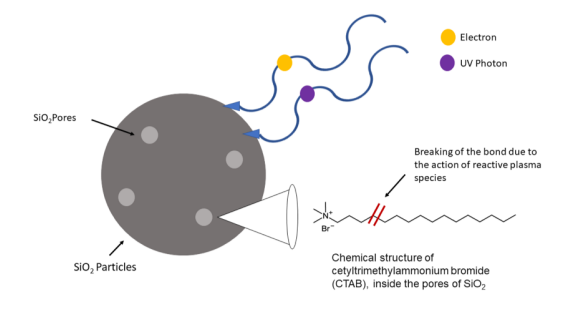

Fig. 8. Proposed mechanism for the removal of CTAB by argon plasma.

Conclusions

The FTIR-ATR, characterization technique showed that both treatments (thermal and plasma) in the SiO_2 particles allowed the decrease in the bands of methyl methylene residues characteristic of CTAB, however plasma was more efficient in the removal of the latest. Also, both treatments increased the particles surface area, volume and pore size, especially when SiO_2 particles were treated at 600 °C and 200 W 1.5 h respectively. However, the thermal treatments fractured the spherical structure of the silica according to the SEM micrographs, while the plasma treatments preserved the co-spherical structure of SiO_2 particles. On the other hand, SiO_2 particles treated at 150 and 200 W had non-hemolytic reaction in all the concentrations tested (1, 2 and 5 mg/mL). It is inferred that the plasma treatment turns out to be more efficient than the thermal treatment in the elimination of this pollutant, since it implies a shorter treatment time and a greater efficiency in the final product, and it does not deform its structure.

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