
Synthesis of silica nanoparticles from sodium metasilicate

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Abstract: A green and facile method to synthesise amorphous silica nanoparticles was performed following principles of sol gel technique, such as the electrolyte's effects on particles morphology. We used sodium metasilicate as safe and biodegradable source of silicon, and two different trisiloxane PEGylated silicon surfactants with different terminal groups to improve micelles formation in a mixture of water ethanol. A low ethanol concentration was used to control condensation rate and a cation exchange resin to control the solution pH and sodium content. The synthesis was based on hydrolysis and condensation reactions, which were lead under vigorous stirring followed by reflux at 95°C for one hour to improve suspension stability and avoid precipitation and calcination steps. Spherical silica nanoparticles were obtained with diameter of 1.66 nm and a negative Zeta potential of 200 mV.

Keywords: silica nanoparticles; sol gel science; sodium metasilicate.

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1 Introduction

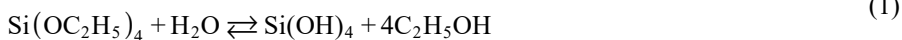
The silicon is found in nature at its stable form bonding with oxygen as silicates or silica in minerals, which together represent 75% of the Earth crust. The atom of silicon belongs to the same family of carbon in the periodic table and shares certain similitude's, such as the capability to form single bonds with four substituent's in tetrahedral configuration. Silicon is less reactive with other atoms of silicon, carbon, nitrogen, or hydrogen; except for the oxygen because of its special affinity. This is due to the electropositivity of silicon. Silicon also shows a special affinity to inorganic compounds rather than organic.

Due to the affinity and thermodynamic stability of silicon-oxygen bonds, silicon-silicate species can be found in a tetrahedral configuration with hydrogen as silane (SiH_4). With oxygen as orthosilicate (SiO_4^{4-}), hydrolysed as orthosilicic acid or silicic acid ($\text{H}_4\text{O}_4\text{Si}$), polymerised within siloxane bonds (Si-O-Si) or as silanol (Si-OH). Also with alkyl substituent's as organosiloxanes and alkoxides as silicones or organosilanes (Brinker and Scherr, 1990; Chen et al., 2009; Craddock, 2018; Iler, 1979; Kappel et al., 2014; Kuroda et al., 2014; Moretto et al., 2000; Pape, 2011).

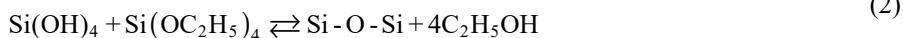
Since Stöber published the first approach in 1968 for the synthesis of silicon nanoparticles (SiNPs) by Sol-Gel method based on the colloidal suspension of particles by repulsive forces synthesised by the condensation of gels into particles. Where the stable suspension of colloidal particles within a liquid is known as sol, and the three-dimensional solid and porous network surrounding the liquid as gel. Their synthesis methods and applications have been studied in several knowledge fields: biomedical, biotechnology, nanotechnology, surface modifications, paints, coatings, cosmetics, agriculture and drug delivery systems. Used for surface modification by hydrophobic silica particle integrated into hierarchical coating to induce hydrophobicity. Modified porous materials for remediation of oil spills in water bodies, dispersant in dry formulations (as powders), and toxin identification by hollow SiNP in lab in paper systems (Chen et al., 2009; Craddock, 2018; Kappel et al., 2014; Kuroda et al., 2014; Moretto et al., 2000; Pape, 2011; Zhang and Cresswell, 2016).

The Stöber method is an approach of Sol-Gel process by the hydrolysis of tetraethyl orthosilicate (TEOS) as silicon source and precursor of silicic acid [equation (1)]. Followed by an alcoholic condensation [equation (2)] catalysed by ammonium hydroxide. Finally the aqueous condensation [equation (3)] in different ratios of distilled water and ethanol as reaction medium in a nucleation reaction (Arkhireeva and Hay, 2003; Bazula et al., 2014; Bogush and Zukoski, 1991; Brinker, 1994; Colaco et al., 2013; Jung et al., 2010; Rahman and Padavettan, 2012; Stober et al., 1968; Widati et al., 2017).

Hydrolysis



Alcohol condensation



Water condensation



Stöber method has been studied and modified to describe the influence of synthesis conditions into the particle's morphology. The shape variation due to protic solvents and its penetration capabilities into the agglomerations improving the formation of siloxane bonds by condensation. This promotes the formation of dense particles in methanol, hollow particles in ethanol and isopropyl alcohol with difference in their thickness coarse being thicker the particles in ethanol (Arkhireeva and Hay, 2003; Bazuła et al., 2014; Bogush and Zukoski, 1991; Colaco et al., 2013; Rahman and Padavettan, 2012; Stober et al., 1968; Widati et al., 2017).

Besides, silicon alkoxides such as TEOS and tetramethoxysilane (TMOS), silicates are widely used as silicon sources, where their main difference are the reaction medium needed. In contrast to silicates, the silicon alkoxides are poorly soluble in water, due to this; protic solvents are commonly used as medium reaction. Other differences are the pH dependence of silicates, which are just stable in a pH range of 8-12.5. This is because when silicate species where near to the Point of Zero Charge (PZC) the counter ion species as sodium promote the coagulation and gelation of silicon species due to the electric double layer compression. This synthesis conditions usually leads the formation of SiNPs with highly negative charge, unless being stabilised by cationic surfactant. In contrast, the synthesis from silicon alkoxides can lead in positive charged SiNPs if the pH is decreased below the PZC. Also, the synthesis from silicon alkoxides requires more parameter control which results in more controllable synthesis products (Arkhireeva and Hay, 2003; Bazuła et al., 2014; Bogush and Zukoski, 1991; Brinker, 1994; Colaco et al., 2013; Jung et al., 2010; Pierre, 1998; Rahman and Padavettan, 2012; Stober et al., 1968; Widati et al., 2017).

In the region where the $\text{pH} \gg \text{PZC}$, the water molecules dissociate faster, increasing the silica solubility, the hydrolysis reaction becomes slower and the monomeric silica species production increases with the condensation rate due the depolymerisation of siloxane bonds. The condensation reactions are favoured by the increase's concentration of deprotonated silica species by nucleophilic attack. In $\text{pH} > 12.5$ mostly silica species are dissolved (Brinker and Scherer, 1990; Brinker, 1994; Gonçalves, 2018; Iler, 1979; Lazaro et al., 2017).

The presence of electrolytes with the protonated state usually defines the synthesis final product. In the acidic conditions the slowly condensation of siloxane bonds lead the formation of small particles, frequently with diameter below 10 nm, where near the PZC the nanoparticle aggregation is favoured and independent of the silicon precursor a three-dimensional network is extend producing SiNPs, branched SiNPs precipitates or a complete gel through the sol. In pH region from 7 to 12.5 without electrolyte species, the nucleation mechanism and Ostwald ripening are favoured, and the nanoparticles could grow until reaching the solubility in particle equilibrium. In presence of electrolytes, the deprotonated silicates and the electronic double layer compression accelerate the condensation, leading in an amorphous three-dimensional network or gel.

Besides Sol-Gel process and Stober method, there are some other methods to synthesise SiNPs, which usually involve the use of potentially toxic solvents and surfactants, with a high time and energy consumption. In contrast with these methods, the Stöber method is one of the eco-friendlier methods. In the research to solve these implications, some authors were opted to study the synthesis parameter, which could lead the synthesis without hazards (Brinker and Scherer, 1990; Gonçalves, 2018; Gorrepati, 2009; Iler, 1979; Lazaro et al., 2017; Schubert 2015; Jung et al., 2010; Zawrah et al., 2009).

Based in Sol-Gel process, we decided to use sodium metasilicate as silicon source because of its economical, biodegradable and safe characteristics. This silicon is adequate for reactions in aqueous medium, saving time and avoiding hazards during the synthesis. In this way, the synthesis route designed and performed here will yield new knowledge about the preparation of SiNPs using sodium metasilicates as silicone source.

2 Materials and methods

2.1 Materials

SiNP were synthesised using sodium metasilicate pentahydrate as silicon source (Metso pentabead 20®, commercial grade), ethanol 99.9% analytic grade (Fermont®). Different ratio mixtures of distilled water (DW) with ethanol were used as reaction medium for hydrolysis. Two different PEGlyated silicon surfactants were included, polyalkyleneoxide modified heptamethyltrisiloxane with hydroxy terminal group (Silwet® L-7608) and a methoxy terminal group (Silwet® L-77) for micelle formation. A cation exchange resin was used to remove the sodium excess in sodium metasilicate solutions (Bulk Reef Supply®) and it was previously washed with 50 ml of ethanol and 50 ml of DW before to use, the other materials were used without any previous treatment.

2.2 Silica nanoparticles synthesis

Previous assays were conducted to determine the synthesis conditions of SiNPs from sodium metasilicate avoiding the use of catalysers, thermal treatments, and re-suspension. The synthesis parameters were selected in function of the precursor concentration, with a supersaturated solution of sodium silicate ranging from 0.175 to 0.3 M. The ethanol/water ratio was from 0 to 1:60 and two pH points far the PZC (4 and 10). The pH adjustment was performed by a cation exchange resin contained in a glass column, passing the silicate solution was according to the desirable final pH (50 g for pH 4 and 30 g for pH 10), the performance of the two silicon surfactants was tested in a final concentrations of 0.33% to 0.62% v/v. Finally, a reflux was performed for 30 min in the temperature range from a 105 to 115°C under constant stirring.

The synthesis of SiNPs began with a silicate solution, followed by the dropwise addition of ethanol under stirring for 15 min, and then the silicate solution was passed through a cation exchange resin volume contained in a glass column. After that, the surfactant solution was added dropwise to the silicate rich species solution in a homogeniser at room temperature and 800 rpm stirring and then was homogenised for 30 min at 2,000 rpm, then, the clear and white suspension was treated by a reflux for 30 min.

2.3 Characterisation

The first synthesis route was defined by the simple observation of the formation of precipitates or gels in the media, where just the samples showing clear suspensions were characterised.

2.3.1 Dynamic light scattering

Dynamic light scattering (DLS) analysis was performed to determine the particle size distribution and stability by Zeta potential before and after each step. The DLS measurements were the first characterisation filter applied to define the synthesis parameters and the addition of reflux as final step. Zeta potential and particle size were measured in a Microtrac® Nanotrac Wave II equipment (Engineering Institute UABC).

2.3.2 Scanning electron microscopy

For morphology characterisation 1 ml of the synthesis suspension was dried at 25°C for 24 h. Scanning electron microscopy (SEM) images were acquired from obtained white powders in an equipment JSM-6010LA (JEOL®) at different magnifications: 100x, 3,000x and 6,000x, with an acceleration potential of 10kV (Engineering Institute UABC). Samples with different amounts of sodium silicate, surfactant, and ethanol: water ratio was observed by SEM after the reflux process to define the optimal synthesis parameters.

2.3.3 X-ray dispersion spectroscopy (EDS)

The semi-quantitative relationship of sodium content with the final morphologies was characterised by elemental microanalysis EDS using a detector coupled to JSM-6010LA (JEOL®) at three different points with acceleration potential of 10kV (Engineering Institute UABC).

2.3.4 Fourier-transform infrared spectroscopy (FTIR)

The functional groups were characterised by IR spectrum of sodium metasilicate, Silwet L-77 and SiNPs acquired from obtained white powders with an equipment Agilent 4300 Handheld FTIR using Attenuated Total Reflectance (ATR), 1 ml of the suspensions was dried at room temperature for 24 h after were synthesised (Industrias Bioquim, S.A. de C.V).

3 Results and discussion

3.1 Dynamic light scattering

The particle size and zeta potential values were obtained by DLS measurements (Table 1). Sodium metasilicate 0.3M solution(A); a silicate solution with sodium ions reduction (B), silicic acid (C), the silicate-silicon emulsions without reflux (D, F and J) and after reflux (E, G and K) and with different silicon surfactants as L-77 for D and E, and L-7608 for H and I.

The sample C showed a significant diminution of zeta potential from the completed dissolved sodium silicate (sample A) in a range from 174.6 mV to 6.5 mV. The evaluation of pH influence in the synthesis showed better results at pH 10 rather than pH 4 with particle size of 1.66 nm and $\zeta = -200$ mV in comparison to 206.3 nm and $\zeta = 12.5$ mV for pH 4 both results after reflux.

Table 1 DLS results

<i>N</i>	<i>Code</i>	<i>pH</i>	<i>D (nm)</i>	ζ (mv)	<i>Polarity</i>	σ ($\mu\text{S}/\text{cm}$)
1	A	14	72.3*	174.6	+	60
2	B	10	84.6	50.5	-	8.365
3	C	4	17.06	6.5	-	90
4	D	10	4.11	0.3	-	3,451
5	E	10	1.66	200	-	4,708
6	F	4	176.6**	15.6	-	64
7	G	4	260.3***	12.4	+	60
8	H	10	156.08	5.1	-	6.207
9	I	10	10.86	32.3	+	2580

Notes: where *n* is for measurement number, *D* is the diameter in nm, ζ is the zeta potential and σ the conductivity.

*Sample A with 79.6% of particles with 72.3 nm and 20.4% of 830 nm.

**Sample F with 96.3% of 176.6 nm and 3.7% of 1.563 nm.

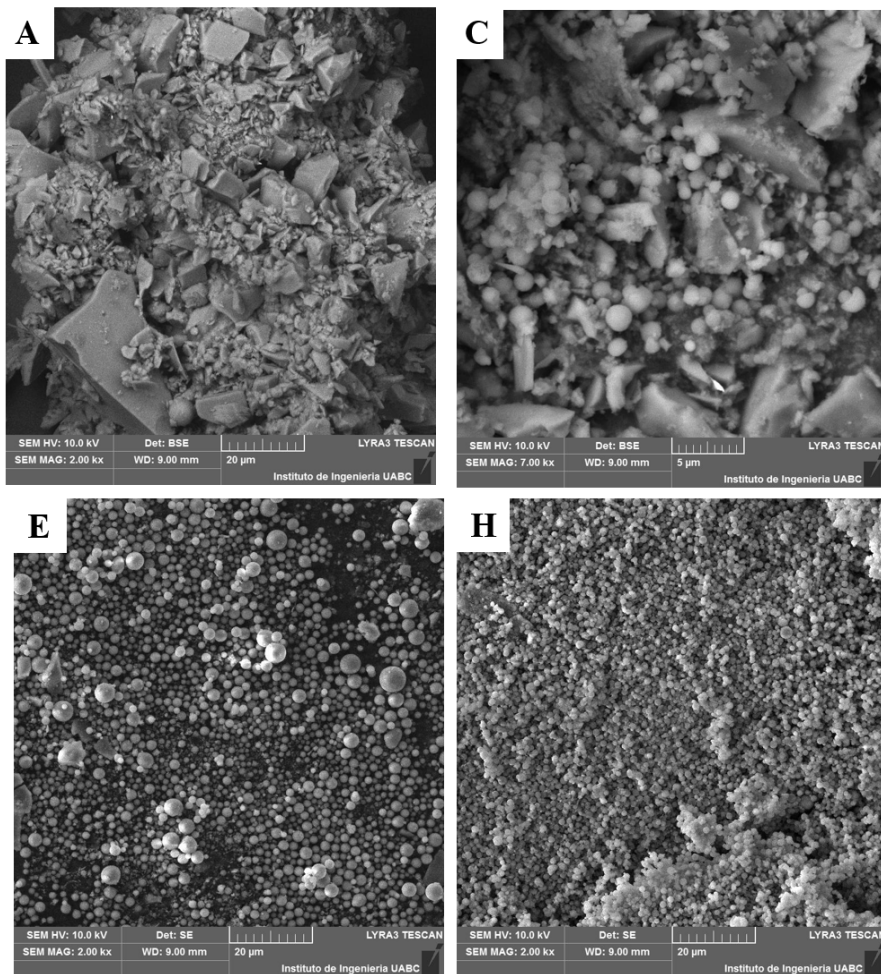
***Sample G with 93.7% of 260.5 nm and 6.3% of 32 nm.

3.2 Scanning electron microscopy

Figure 1 shows the SEM images for the synthesis of products in the parameters defined by DLS as pH 10, ethanol: water ratio 1:60 and with the silicon surfactant Silwet L-77®. The study in SEM was carried out to know the final particle morphology according to the ethanol, surfactant, and precursor concentration. The sample A corresponds to the sample with ethanol excess with an ethanol: water content up to 1:0.8, the sample C was synthesised in the absence of ethanol, the samples E and H were synthesised with ethanol: water ratio of 1:30, varying the surfactant concentration from 0.33% v/v to 0.62% v/v respectively.

Our results have coincidence with those reported by Jung et al. (2010). They began the condensation of silicates species by adding alcohols with different polar length. They also show how the different alcohols as methyl, ethyl and isopropyl can lead into different particles morphology dense and hollow respectively with more thickness in the case of ethyl alcohol. This is related to the alcohol's capacity to impregnate the micelles in dependence of their polar chain length improving a uniform water and alcohol condensation reactions from the shell to the core. In addition, their groups treated with different washing solvents resulting in hollow particles with water and solid structures with alcohols (Jung et al., 2010).

Figure 1 SEM images from SiNPs with ethanol: water ratio 1:0.8 (a), with ethanol absent (c), and e and h with ethanol: water ratio near 1:60 in Silwet total concentration about 0.33% v/v and 0.62% v/v



3.3 X-ray dispersion spectroscopy (EDS)

In Figure 2, SEM images with their respective EDS for the samples A, C, E and H are shown. We can see the relationship of the remanent sodium content and the spherical uniform shape that shows absence of sodium in contrast with the amorphous structures which showed the presence of sodium.

The SEM-EDS results coincides with the polymerisation theory (Figure 4), where the presence of electrolytes in both in acidic or alkaline conditions enhance the gel formation by the electrical double layer compression improving the formation of siloxane bonds, while in alkaline conditions and in absence of electrolytes can be obtain an stable SiNPs sols (Brinker and Scherer, 1990).

Figure 2 EDS results from SiNPs with ethanol: water ratio near 1:0.8 (a), with ethanol absent (c), and e and h with ethanol: water ratio near 1:60 in Silwet total concentration about 0.33% v/v and 0.62% v/v (see online version for colours)

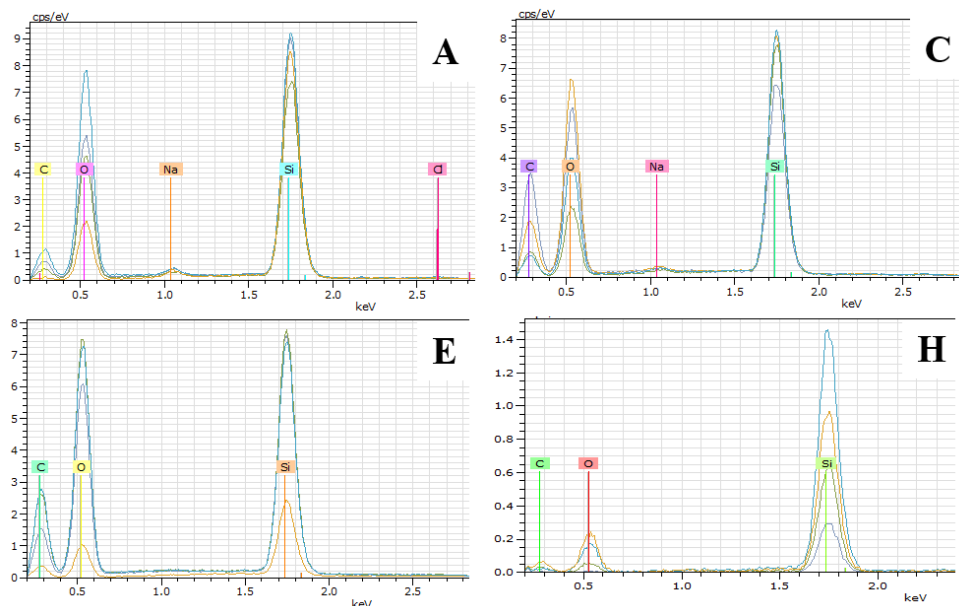
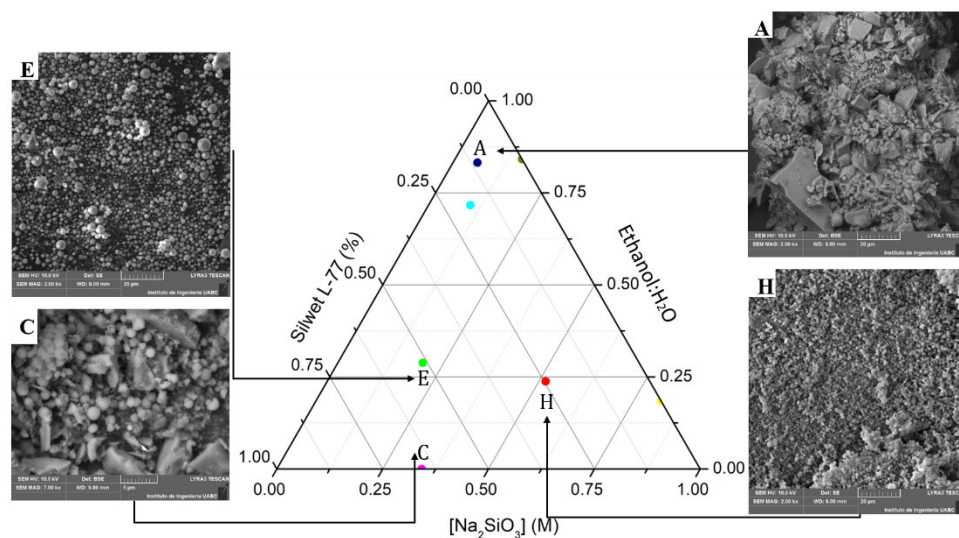


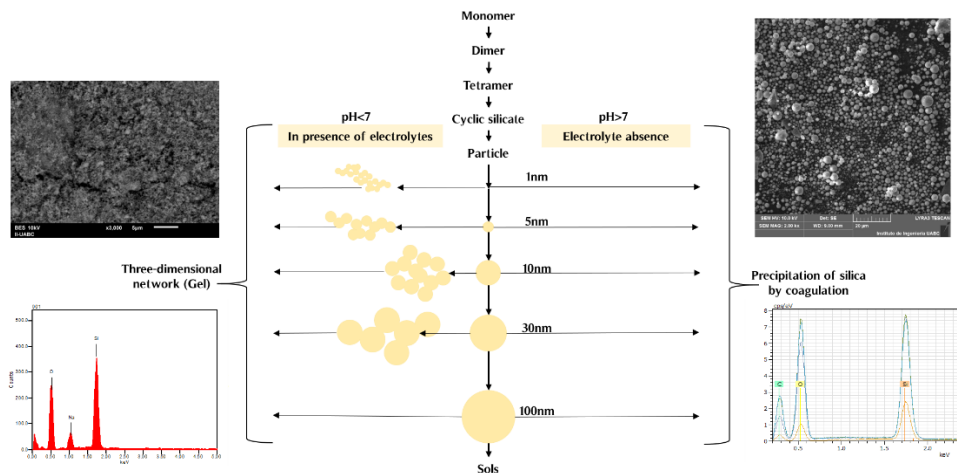
Figure 3 Trifasic diagram where were related the synthesis parameters with the obtain morphologies by SEM (see online version for colours)



In Figure 3, it can be appreciated in A how the excess of ethanol and the lower surfactant content enhance the condensation rates reliable with the tridimensional gelation through the media, in sample C is showed how the absence of ethanol lead a non-uniform condensation reaction resulting in a mixture of amorphous and spherical particle shape.

In contrast, the point E, which has the same precursor, amount of C but with ethanol: water ratio near to 0.3 presents uniform spherical particles. Finally, the ethanol: water ratio could be rectified with the point H where the ethanol: water ratio was maintained resulting in the same spherical morphology.

Figure 4 Relationship of the polymerisation theory in sol gel science with electrolyte content during the sinps synthesis (see online version for colours)



Source: Brinker (1994), Brinker and Scherer (1990), Iler (1979) and Ulrich (2015)

3.4 Fourier-transform infrared spectroscopy (FTIR)

In Figure 5, it can be seen the IR spectra of sodium metasilicate with the characteristic peaks of water molecules at 2,885 cm^{-1} and 1,142 cm^{-1} . This is due their pentahydrate pristine form, the stretching vibrations of silanol groups (Si-OH) at 964.5 cm^{-1} and the symmetric and asymmetric vibrations of siloxane bonds (Si-O-Si) at 822.8 cm^{-1} and 677.6 cm^{-1} (Arkhireeva and Hay, 2004; He et al., 2015; Sarawade et al., 2011; Sumathi and Thenmozhi, 2015; Zulfiqar et al., 2016).

Figure 5 Sodium metasilicate IR spectrum (see online version for colours)

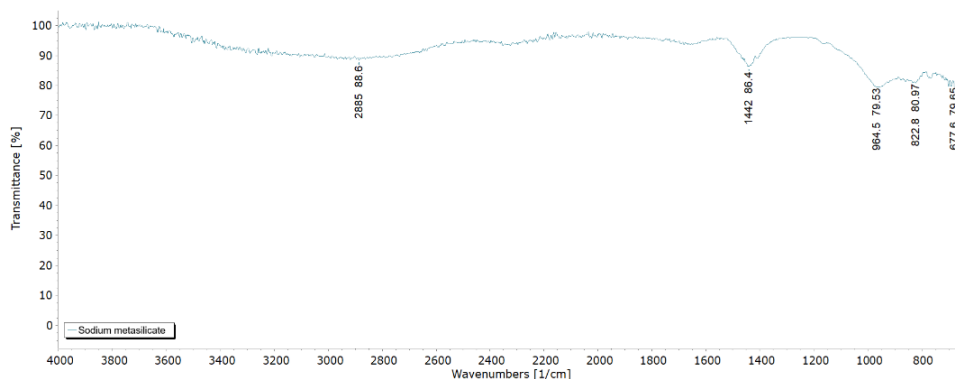


Figure 6 shows the IR Spectrum of the trisiloxane PEGylated silicon surfactant (Silwet L-77), that shows the best results in DLS and SEM-EDS characterisation. It can be observed the characteristic stretching vibrations of C-H bonds at $2,868\text{ cm}^{-1}$, $1,455\text{ cm}^{-1}$, $1,350\text{ cm}^{-1}$ and 752 cm^{-1} . Also the Si-C vibration related to the functional group CH_3 in silsesquioxanes at $1,252\text{ cm}^{-1}$ and 837 cm^{-1} , and the siloxane vibration at $1,036\text{ cm}^{-1}$ (Arkhireeva and Hay, 2004; Chapa et al., 2018; He et al., 2015; Parale et al., 2012; Sarawade et al., 2011; Sumathi and Thenmozhi, 2015; Zulfiqar et al., 2016). The SiNPs showed in Figure 7 indicates the slightly presence of C-H and Si-C at $2,868\text{ cm}^{-1}$ and $1,252\text{ cm}^{-1}$ related to the functional groups of the trisiloxane PEGylated surfactant. A strong symmetrical and asymmetrical vibrations of siloxane bonds at $1,029\text{ cm}^{-1}$ and 793.1 cm^{-1} are also showed (Arkhireeva and Hay, 2004; Chapa et al., 2018; He et al., 2015; Sarawade et al., 2011; Sumathi and Thenmozhi, 2015; Zulfiqar et al., 2016).

Figure 6 Trisiloxane PEGlyted silicon surfactant (Silwet L-77) IR spectrum (see online version for colours)

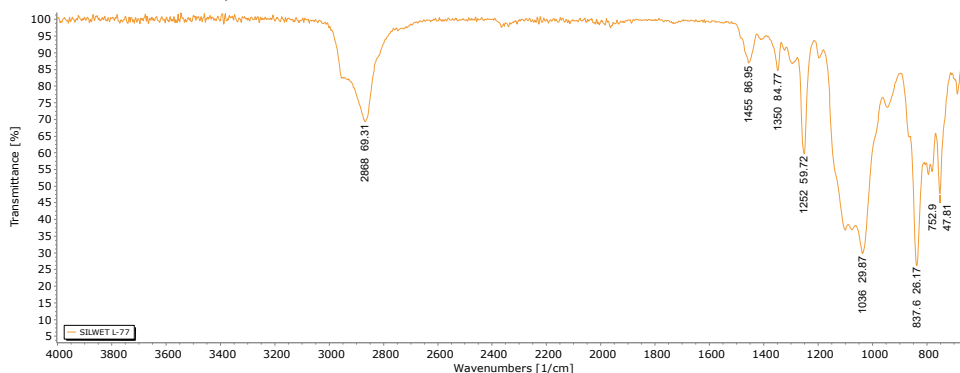
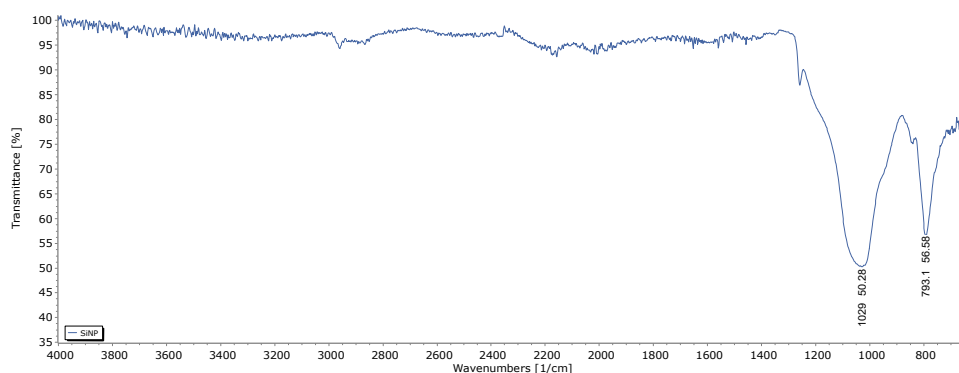


Figure 7 Silica nanoparticles IR spectrum (see online version for colours)



4 Conclusions

Spherical silica nanoparticles were obtained by an alternative green and eco-friendly method based on Sol-Gel principles, by DLS results the SiNPs parameters were determined where the samples with pH 10 shows smaller particle size than the particles synthesised in pH 4 and better stability with zeta potential nearly to the negative limit.

After reflux, the samples with pH 10 showed better results diminishing their particle size and increasing the zeta potential. With the SEM and EDS results a relationship between pH and remnant sodium was achieved with their final structures and elemental composition. Based on the FTIR analysis was determined the final synthesis route without catalyse, large amounts of alcohol and hazard silicon source, just based in the Sol-Gel principles and avoiding unstable silicon condition as gelation at pH near the PZC or the excess of electrolytes.

The SiNPs with high negative charge are useful in surface modification applications or functionalisation by electrophilic attack due to its tendency to make covalent bond with hydroxyl rich surface and to react with metal cations, respectively making the SiNPs suitable to create antibacterial coating, as carriers in nanomedicine, nanopesticides or nanofertilisers.

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