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SYNTHESIS AND PROPERTIES OF ORGANOSILICA PARTICLES WITH QUATERNARY AMMONIUM BEARINGS AS BACTERIOSTATIC INTERFACES

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In this study, bacteriostatic interfaces tested against Gram-negative bacteria (GNB) were developed. For this purpose, quaternary ammonium-based organosilica microparticles with cethyl trimethyl ammonium bromide (CTAB) and vinyl benzyl trimethyl ammonium chloride (VBTAC) were synthesised. The modified silica microparticles were subjected to physical-chemical characterization via Fourier Transform Infrared (FTIR) spectroscopy, Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), porosimetry (BET) and Dynamic Light Scattering (DLS) measurements. The QAS-modified silica particles have proven to have newsworthy microbial inert effect against E. Coli O157 and total Coliformi bacteria.

Keywords: organosilica, QAS, Gram-negative bacteria, bacteriostatic effect

1. Introduction

In recent decades, infections by pathogenic microorganisms have become a frightening health and social issue worldwide. Annually, one quarter of the

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global deaths is caused by diseases triggered by germs (bacteria, fungi, viruses etc). Since the so-called “superbugs” exist everywhere and can be spread through air, water, food and soil, the prevention and treatment of microbial infections becomes a massive challenge [1-3]. World Health Organization (WHO) experts released a global strategy for containment of antimicrobial-resistant microorganisms, including simple measures as hand-washing and food hygiene [4]. However, the water quality is also very important for human health and the presence of pathogenic bacteria becomes a real issue. Moreover, the wastewaters (domestic and industrial) are contaminated with antibiotics, disinfectants and antiseptics leading to more resistant pathogens [5].The majority of pathogens responsible for water contaminations originate from faecal contamination because of insufficient treated water. Generally, the infections react against with conventional antimicrobial agents based on natural or low-molecular-weight compounds, being susceptible to their action [6]. Hence, their difficult elimination is the result of bactericidal diffusion leading to environmental contamination. To address this challenge, antimicrobial polymers are promising materials to combat bacterial pathogens, in terms of enhanced antimicrobial efficacy, reduced toxicity and prolonged lifetime [7]. Considering their sustainable and environmentally friendly properties for wastewater decontamination, antimicrobial polymeric materials present a wide range of applications in medicine, household, food packaging and storage, water purification systems, etc. In the last decade, one of the most effective and widely used types of antibacterial materials is quaternary ammonium-based polymer salts [8].

Since their discovery in 1935, quaternary ammonium salts (QAS) with different formulations have been explored as disinfectants; recently, they are used for industrial purposes, antifungal treatment in horticulture and water and wastewater treatment [9-13]. The antimicrobial activity of QAS confers lipophilicity, being a function of the N-alkyl chain length. The optimal activity against Gram-positive bacteria (GPB) is achieved with when using QAS with chain lengths of 12–14 alkyls, whereas the optimal activity for Gram-negative bacteria (GNB) when using 14–16 alkyls. QAS with N-alkyl chain lengths <4 or >18 are virtually ineffective [14]. Considering the fact that GNB structure has three layers including an outer membrane with a toxic component named lipopolysaccharide (LPS) that acts as a barrier against QAS-based biocides, GNB are more resistant than GPB [15]. The antimicrobial effect refers to an interaction between the positively charged quaternary nitrogen of the QAS and the negatively charged head groups of acidic phospholipids in bacterial membranes. In addition, surfaces containing QAS groups damage pathogenic GNB bacteria cells by disruption of their membrane integrity and leakage of cellular content [16, 17]. Very recently, a report revealed that the exposure of bacteria to QAS can lead to proliferation of antibiotic resistance genes (ARG) [18]. Hence, efforts must be constantly done to prepare other types of QAS surfaces to reduce microbial effects of GNB.

The versatility of the sol-gel method allows us to design unique properties of materials at low temperatures compared to other polymerization techniques. The sol–gel process normally requires molecular precursors, this allowing the preparation of a broad range of organically modified silicate systems by mixing more than one precursors. The two steps of a sol-gel reaction depend on several process parameters e.g. pH, type and concentration of catalyst used for the hydrolysis, reaction temperature, time of heating, nature of the pendant groups, and solvent's nature. It can be noted, that these variables have a strong influence upon the fundamental characteristics of sol-gel materials such as homogeneity, porosity, refractive index, surface, mechanical properties and thermal stability [19, 20].

In this context, despite numerous studies over many years, the preparation of organosilica particles via sol-gel method based on QAS groups (i.e. cethyl trimethyl ammonium bromide (CTAB) and vinyl benzyl trimethyl ammonium chloride (VBTAC) used for bacteriological or medical applications is still a new topic in this field [21-23]. Previous studies have shown that CTAB is one of the most frequently overused QAS cationic surfactant for the synthesis of mesoporous silica particles, considering its strong bactericidal potential. Jin et al. showed an efficient Gram-negative *Escherichia coli* inactivation by CTAB magnetic nanoparticles within 60 min [24]. A recent study of Cihanoğlu and Altinkaya [25] described the preparation of CTAB-containing polysulfone-sulfonated polyethersulfone (PSF-SPES) based ultrafiltration membranes with antibacterial properties. In another report, A. Abduraimova and colleagues attached spherical shaped Ag nanoparticles on the surface of CTAB-loaded mesoporous silica nanoparticles, leading to synergetic antimicrobial activity against E. coli and S. aureus bacterial strains [26]. Nevertheless, few reports dealing with VBTAC for delivering quaternary ammonium-functionalized particles against pathogenic bacteria have been published in the literature [13]. In a study by Kougia et al. [27], the combination of the hydrophilic monomer acrylic acid (AA), at low contents, with the covalently attached bacteriostatic group vinyl benzyl dimethylhexadecylammonium chloride (VBCHAM) resulted in a high bacteriostatic activity against P. Aeruginosa and E. Faecalis. With regard to the recent literature, this study provides a simple and low-cost procedure to prepare QAS-modified silica microparticles as bacteriostatic interfaces, with the use of sol-gel derived techniques. The role of the QAS nature upon organosilica properties with bacteriological inert effect against E. Coli O157 and total Coliformi bacteria has never been studied elsewhere.

In line with the stated issues, we present in this work a simple and low-cost sol-gel derived method for obtaining organosilica microparticles successfully modified with two types of QAS, namely CTAB and VBTAC. Morphological, structural and thermal studies were undertaken to assess the effect of monomers and surfactants bearing QAS upon the overall properties of prepared QAS derived interfaces. To the best of our knowledge, the organosilica particles with QAS bearings and with either vinyl or phenyl organic moieties (derived from organosilanes) displaying microbial inert effect against E. Coli O157 and total Coliformi bacteria is reported herein for the first time.

2. Experimental section

2.1. Reagents and chemicals

Functional monomers tetraethoxy silane (TEOS, 98%, Fluka, Fluka Chemie GmbH, Buchs, Switzerland), vinyl triethoxy silane (VTES, 99%, Fluka, Fluka Chemie GmbH, Buchs, Switzerland) and phenyltriethoxy silane (PhTES, 99%, Fluka, Fluka Chemie GmbH, Buchs, Switzerland) were used as the oraganosilica monomers. Stabilizers cethyl trimethyl ammonium bromide (CTAB, 98%) and vinyl benzyl trimethyl ammonium chloride (VBTAC, 98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Solvents ammonium hydroxide (NH_4OH, 25 %, ChimReactiv, (Ion Creanga, NT, RO), ethanol (EtOH, 99.6 %, Fisher Chemical, Fisher Scientific, Pittsburgh, PA, USA) and lab distilled water were used as such. Initiator 2,2'-Azobis(2-methylpropionamidine dihydrochloride (AIBA, 98%) was supplied by Sigma-Aldrich (St. Louis, MO, USA) and used for the concurrent radical polymerization of VBTAC. For the microbiological analysis, filter funnels with 47 mm diameter filtration and PES membrane (PALL filters 516-0427), *E coli O157* and coliforms chromogenic agar plates, TSC agar plates (Sanimed International, Romania) were used.

2.2. Synthesis of organosilica particles modified with QAS

Three organosilica systems were synthesized by sol-gel techniques similar to that described by Yague et al. [28] using TEOS as structural monomer, VTES or PhTES as functional monomers and CTAB as stabilizer (noted TEOS/PhTES/CTAB, TEOS/VTES/CTAB and the reference TEOS/-/CTAB). Briefly, a typical run consisted in mixing two solutions at room temperature (25 °C), one containing the precursor gel and the other the catalytic medium. The precursor gel solution contained the functional monomer TEOS (2.4 mol * 10^{-2} or 4.8 mol * 10^{-2}), the co-monomer VTES or PhTES (2.4 mol * 10^{-2}) and the stabilizer CTAB (1.44 mol * 10^{-3}) dissolved in ethanol (2.78 mol). The catalytic medium contained 25% ammonium hydroxide solution (25% NH_4OH/ H_2O, 1/5, mol/mol). The compositions in molar ratios of organosilica particles prepared via sol-gel method are presented in Table 1. The precursor solution was gradually added to the catalytic medium at room temperature (25 °C) and stirred at 200 rpm for 2h for partial hydrolysis of the -OR groups of the monomers followed by aldol polycondensation. The fourth organosilica system, noted TEOS/VTES/VBTAC, was prepared in similar conditions with the difference that the precursor solution contained VBTAC (4.7 mol * 10^{-3}), instead of CTAB, and was gradually added to the catalytic medium at 65 °C for a whole reaction time of 4.5 h. For this latter recipe, AIBA (7.37 mol * 10^{-4}) was used as radical initiator for the concurrent polymerization reaction of VBTAC and VTES in the attempt to yield interpenetrated networks according to Florea et al. [29]. The particles were washed in mild conditions (2 x 250 mL of distilled water) in order to remove only the residual monomers (but not the stabilizer, in CTAB-based organosilica) and separated by centrifugation. TEOS/VTES/VBTAC samples were grinded to yield submicronic particles before analysis, as robust chunks of polymers were obtained after radical polymerization. The washed particles were dried at room temperature for one week and then in a vacuum oven for 24 hours at 80 °C until constant weight.

Table 1

Composition of the organosilica particles modified by QAS

Polymer	Molar ratio TEOS/RTES/ QAS	Molar ratio TEOS/EtOH
TEOS/PhTES/CTAB	1/1/0.06	0.1/11.6
TEOS/VTES/CTAB	1/1/0.06	0.1/11.6
TEOS/-/ CTAB	1/-/0.03	0.1/5.7
TEOS/VTES/VBTAC	1/1/0.2	0.1/11.6

2.3. Characterization methods for the QAS-based organosilica particles

The prepared particles were characterized morphologically, structurally and thermally using various instruments and methods. Fourier-Transformed Infrared Spectroscopy (FTIR) measurements (Bruker Tensor 37, 400-4000 cm^{-1} range, with a resolution of 4 cm^{-1} and a number of 16 scans) were used to highlight the composition and chemical bonds of microparticles. Thermogravimetric analysis (TGA) was performed using TA Q5000 IR Thermogravimetric Analyzer in nitrogen at a heating rate of 10 °C/ min (from room temperature to 700 °C). Thermal stability of polymers was studied to highlight the effect of monomers and stabilizers upon the organosilica materials, as complementary method for FTIR analysis. The surface morphology, the shape and size of microparticles was highlighted by SEM (ESEM - FEI Quanta 200, Philips) under the following conditions: ambient, LFD at 5 μm resolution. Particle size analysis was performed by dynamic light scattering (DLS, Zetasizer Nano ZS System) (Malvern International Ltd.) using 0.04 g of the sample diluted in 25 ml distilled water. The agglomeration rates were calculated as follows: average size of aggregates (DLS)= mean particle size (SEM)/ mean size of aggregates (DLS). Prior to adsorption-desorption measurements in N_2, samples were degassed at 373.15 K for 3h under vacuum (p <102 Pa) to eliminate adsorbed gas and moisture. Further on, the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods have been used to measure the specific surface areas as well as the pores volume and pore size distributions. All adsorption-desorption isotherms were acquired at 77.4 K (-196 °C) using a Quantachrome Nova2200e Analyzer (Quantachrome Instruments USA).

2.4. Bacteriological activity tests

The research study on the efficiency of the prepared materials was assessed using samples of wastewater with 90% industrial and 10% domestic charge, containing GNB. Wastewater (WW) samples have been collected from the influent of one wastewater treatment station (homogenization basin) and transported to the laboratory in the same day, in proper shipment conditions. The bacteriological indicators of wastewater alone were considered “control” values for the following analysis of microparticles.

The WW samples were analyzed as received and after direct contact with the organosilica particles (0.5 g). A total period of 24 h contact time was chosen for all the experiments and the volume of WW for testing the particles was 100 ml/ sample. After 24 h, the WW supernatant from the sample was collected, after sedimentation of microparticles, in a clean vessel and filtered using conventional membrane filtration methods. In order to evaluate the efficiency of the organosilica particles, the PES-membrane filters were used for determining bacteriological indicators and their values were compared with those obtained for WW control sample. In this respect, conventional membrane filtration methods EPA 1603/2009 and EPA 1600/2009 (versions of standard method ISO 9308-1: 2015, applicable to WW with high bacterial content) were used for all determinations. For performing the bacteriological analyses, the PES-membrane filters were placed on agar plates to be ensured that no air bubbles were trapped between the membrane filter and the medium. Filter disks were transferred to the chromogenic/agar plates and incubated at 44 °C± 0.5 °C for 24 h (Hach Incubator). The results were read within 15 minutes after removing the plates from the incubator. The colonies were counted using a colony counter (Funke Gerber).

3. Results and discussion

3.1. FT-IR measurements of microparticles

Comparing the FTIR spectra of all organosilica microparticles (Fig. 1), some similarities were observed. Characteristic bands of the organic–inorganic matrix formed during polycondensation and radical polymerization were identified in the spectra. The absorption peaks observed in the 3731-3745 $cm^{-1}$and 3421-3433 cm^{-1} regions (intense and broad bands) are attributed to O-H stretching vibration due to physisorbed water. However, in the spectrum of TEOS/VTES/VBTAC (fig. 1d), the –OH bands may overlap with the characteristic υ_{-NH_2} and υ_{-NH_3} bands recorded in the 3400-3500 cm^{-1} range.

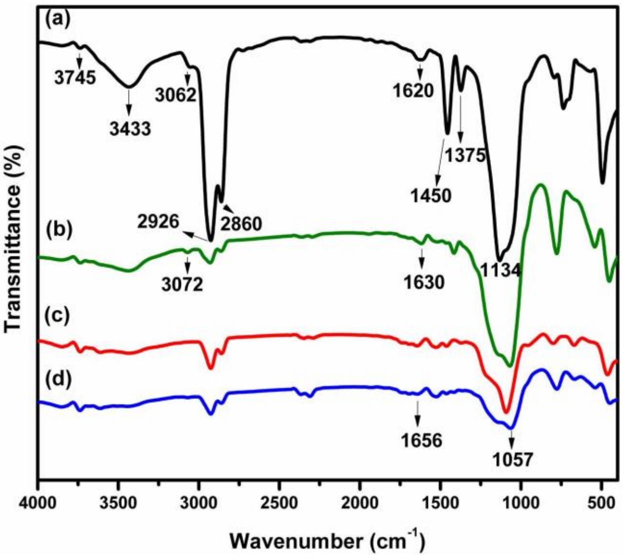

Fig. 1. FT-IR spectra of organosilicas modified with QAS (a) TEOS/PhTES/CTAB (b) TEOS/VTES/CTAB (c) TEOS/-/CTAB (d) TEOS/VTES/VBTAC

In the spectra, υ_{CH} (vinyl from VTES, phenyl from PhTES), υ_{CH2}(vinyl from VTES, methylene from CTAB) and $\upsilon_{(SiO)n}$ vibrations, assigned to the organic moieties and the hybrid backbone of VTES, PhTES and TEOS monomers, respectively, were registered in the 2854–2862 cm^{-1}, 2926–2933 cm^{-1} and 1134–850 cm^{-1} wavenumber region, respectively. The υ_{CH3} [H_3C-$(CH_2)_{15}$ from CTAB] was observed around 3070 cm^{-1}, only in the spectra of TEOS/PhTES/CTAB and TEOS/VTES/CTAB, assuming that in the reference (Fig. 1c) CTAB was washed quantitatively. In the spectra of TEOS/PhTES/CTAB, the band recorded at around 1620 cm^{-1}, characteristic for $\upsilon_{-C=C}$ in the phenyl group, can be observed. For TEOS/VTES/CTAB-based organosilica (fig. 1b), a faded band appeared at 1630 cm^{-1}, characteristic to vinyl bonds in VTES. This band is not present in TEOS/VTES/VBTAC as the vinyl groups are consumed during radical polymerization with VBTAC. The stretching vibrations of the C=C bonds corresponding to the aromatic nucleus from VBTAC were registered around 1656 cm^{-1} in the sprectrum of TEOS/VTES/VBTAC (fig. 1d-faded band). Additionally, the presence of bands with increasing intensities at 2300 cm^{-1} and 2380 cm^{-1} observed in all the spectra can be assigned to the ammonium group $N^+(-CH_3)_3$ [29].

3.2. Thermal stability of QAS-modified microparticles

The thermal degradation behaviour of the microparticles based on QAS was performed to identify certain differences that may quantify the effect of the monomer and the stabilizer upon the polymeric structure as well as to determine the thermal stability of the analyzed materials. Fig. 2 shows the TGA and DTG curves of QAS- modified microparticles. The studied degradation range of the polymers was 20-700 °C, because the organic fragments of interest, i.e. the vinyl, phenyl and QAS groups degrade at low temperatures. It can be seen that all particles present different degrees of stability. All the microparticles begin their degradation around 150 °C (due to the presence of stabilizers). Based on Fig. 2 (b), the first stage of mass loss occurred at maximum temperatures ranging from 204 to 244 °C, which may be attributed to degradation of monomers and stabilizers moieties, in the form of formyl, acetyl or ammonium, whereas between 400 and 700 °C the rest of the organic, in the form of methyl, acetylene or amine moieties decomposed completely [30].

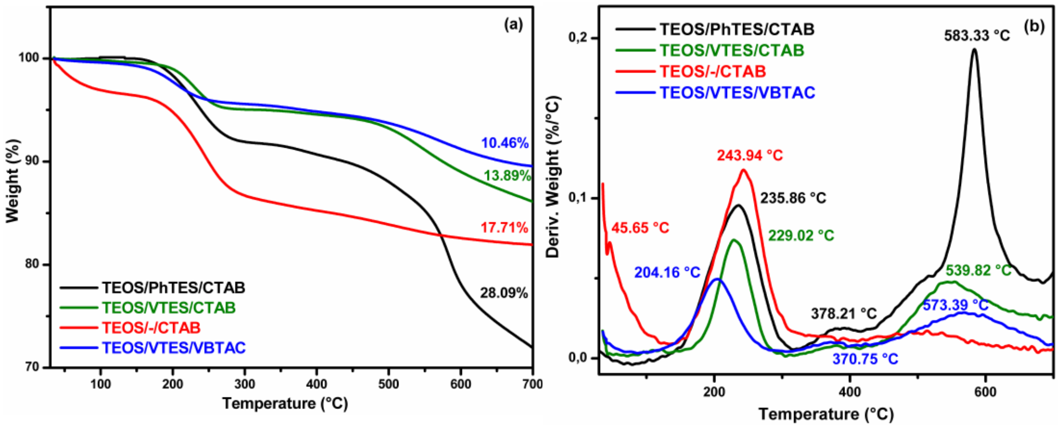

Fig. 2. TGA (a) and DTG (b) curves of TEOS/PhTES/CTAB-based organosilica, TEOS/VTES/CTAB-based organosilica; TEOS/-/CTAB-based organosilica and TEOS/VTES/VBTAC-based organosilica particles

However, TEOS/VTES/VBTAC microparticles exhibited somewhat higher thermal stability than those based on CTAB, probably due to the supplementary crosslinking nods formed during the concurrent radical polymerization. This assumption was based on the fact that the residue amount recorded for this sample was around 90 wt.%, registering the lowest mass loss in the series.

3.3. Particle size and morphology

Dynamic light scattering (DLS) measurements used to determine the particle size distribution and zeta potential of the samples are shown in Fig. 3. It is relevant to note that the particle size is quite an important factor that can significantly affect the bactericidal effect of organosilicas. All organosilica particles exhibited unimodal curves in the 0-2000 nm range, with rather narrow polydispersities and with mean particles sizesunder1700 nm. The mean particle size registered for TEOS/PhTES/CTAB microparticles was around 1628 nm (Fig. 3 a), while for TEOS/VTES/CTAB microparticles about 1684 nm (Fig. 3 b), but with a major representative peak at 334 nm. A significant decrease of the mean size for TEOS/-/CTAB (192 nm) was observed (Figs. 3 c and d), as it contains no other organic moiety to alter the hydrodynamic diameter of the particle. Further on, the fact that TEOS/VTES/VBTAC polymers were grinded before analysis has led to some major errors of the mean particle size (the analyzed particles being around 324 nm with a major peak at 93 nm). In addition to particle size distributions, Zeta potential measurements were recorded for each sample at the same time. The results indicated that the Zeta potentials of the particles were −2.49 and −18.1 mV for TEOS/PhTES/CTAB and TEOS/VTES/CTAB microparticles, respectively. The particles show a quite strong negative Zeta potential, but mostly due to the electrostatic charge brought by the free vinyl or phenyl groups, at the surface, which are in little extent balanced by the ammonium groups of CTAB. On the other hand, the Zeta potential records showed positive values for TEOS/-/CTAB (7.94 mV) and TEOS/VTES/VBTAC microparticles (8.83 mV), indicating the presence of QAS groups as well.

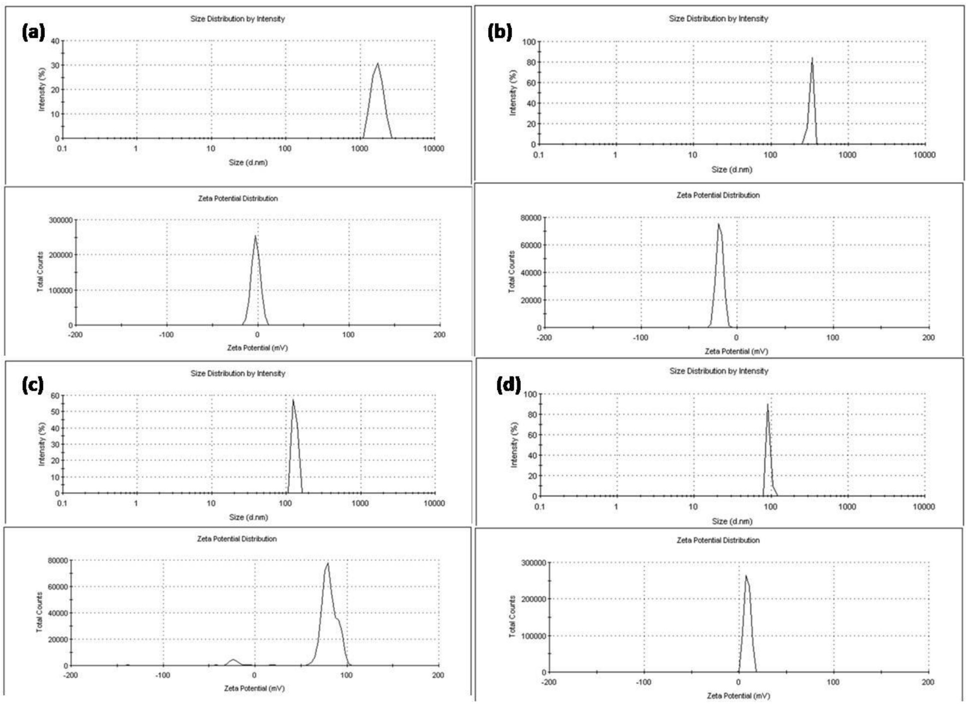

Fig. 3. Dimensional distribution and zeta potential of organosilica particles: (a) TEOS/PhTES/CTAB-based organosilica; (b) TEOS/VTES/CTAB-based organosilica; (c) TEOS/-/CTAB-based organosilica and (d) TEOS/VTES/VBTAC-based organosilica.

By comparing the morphology of the four types of QAS-modified microparticles, significant differences in particle shape and size occurred due to (co-) monomers and / or stabilizers with QAS. SEM images were conclusive and sustained the statements provided so far. TEOS/PhTES/CTAB microparticles presented homogeneous and spherical morphologies with smooth surfaces (Fig. 4 a), which confirmed the lower polydispersity index (PdI = 0.1) registered by DLS. For TEOS/VTES/CTAB microparticles, a similar homogenous and spherical shaped morphology of nanoparticle aggregates (submicronic) was observed (Fig. 4 b); however, large size agglomerates were also formed (with Pdl=1). Further on, SEM images of TEOS/-/CTAB particles fit well with DLS results in terms of submicron particle size and polydispersity index (Pdl=1), showing a coalescence phenomenon.

Different from the particles systems based CTAB, the microparticles based on TEOS/VTES/VBTAC, obtained by sol-gel reaction and parallel radical polymerization (Fig. 4 d), exhibited robust particles with irregular shapes and sizes due to grinding (herein, the fraction remaining after sieving the submicronic fraction was analyzed), with alternating submicronic-micronic particles and quite low polydispersity index (PdI = 0.4), as previously reflected by DLS analysis.

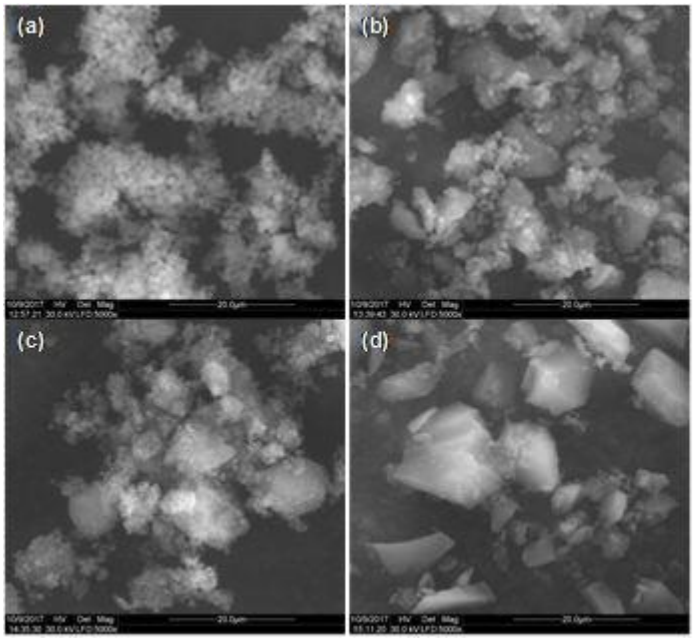

Fig. 4. Morphology of (a) TEOS/PhTES/CTAB-based organosilica; (b) TEOS/VTES/CTAB-based organosilica; (c) TEOS/-/CTAB-based organosilica and (d) TEOS/VTES/VBTAC-based organosilica particles, at 20 μm

3.4. Porosimetry measurements

The N_2 absorption-desorption isotherms (Fig. 5) using the BET method allowed the measurement of BET specific surfaces area, pores volume (Vp), pore specific surface area (S_{BET}) and pore average diameter (Dp) of synthesized QAS microparticles (values presented in Table 2). According to IUPAC definition [31], the adsorption-desorption isotherms described a type IV behavior, indicating that all particles were mesoporous. The values attained for the average pore diameter (ranging from 1 to 29 nm), the BET specific surface area (from 3 to 264 m^2/g) and the total pore volume (0.01 - 0.8 cm^3/g) highlighted major differences between the synthesized microparticles systems, mainly due to the nature of involved organosilanes and stabilizers but also to the synthesis approach. One may notice from Table 2 that the TEOS/VTES/CTAB and TEOS/VTES/VBTAC microparticles exhibited the highest values for specific surfaces area and pore volume, which indicated that VTES may play a more important role in this equation regardless of the synthesis approach. It seemed like the use of CTAB stabilizer resulted in a higher specific surface area for TEOS/VTES/CTAB, at the expense of using VBTAC for TEOS/VTES/VBTAC. However, this difference may also be the result of denser networks formed during radical polymerization of VBTAC and VTES.

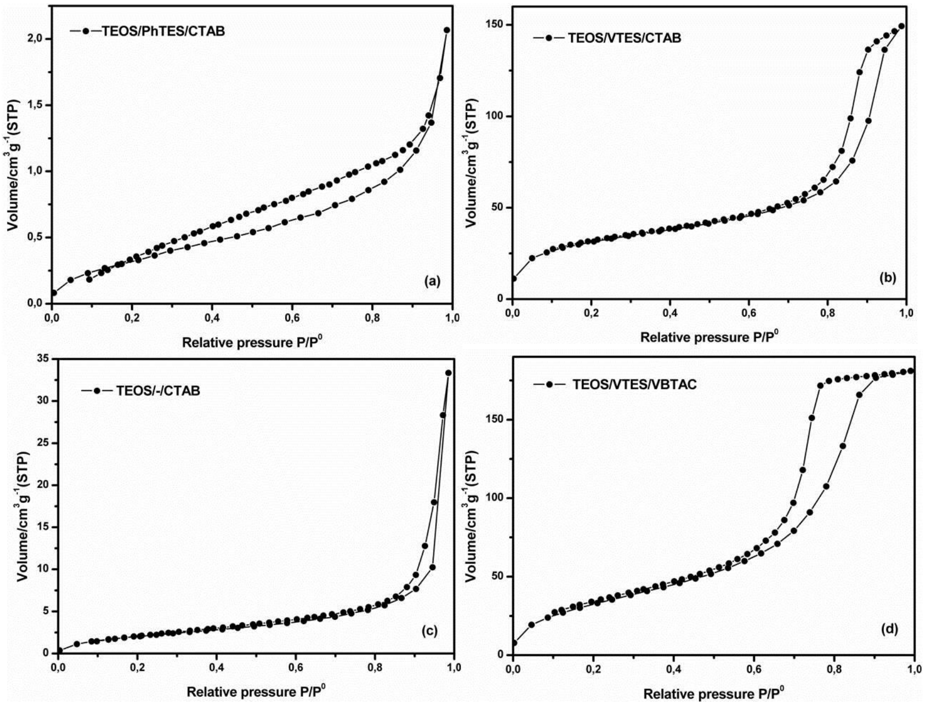

Fig. 5. Nitrogen adsorption/desorption isotherms at 77 K for (a) TEOS/PhTES/ CTAB, (b) TEOS/VTES/ CTAB, (c) TEOS/-/ CTAB and (d) TEOS/VTES/ VBTAC

Table 2

Nitrogen adsorption-desorption summary on organosilica microparticles

Polymer	BET Surface Area [S_{BET} (m^2/g)]	D_p (nm)	V_p (cm^3/g)
TEOS/PhTES/ CTAB	3.41	2.77	0.01
TEOS/VTES/ CTAB	263.51	1.54	0.82
TEOS/-/ CTAB	35.49	28.75	0.25
TEOS/VTES/ VBTAC	225.55	6.81	0.68

The suggested explanation was also supported by the presence of a well-defined stage in the absorption-desorption curves, registered for TEOS/VTES/CTAB (Fig. 5, b) and TEOS/VTES/ VBTAC (Fig. 5, d).This stage between the relative pressure values (P/P0) of 0.1 and 0.7 indicated the filling of mesopores with N_2 gaseous molecules. The higher the relative pressure values the higher the surface area, pore surface area and/ or pore volume, as more N_2 is needed to fill out the voids. A wide relative pressure range was also observed for TEOS/-/CTAB microparticles, with threshold at over 0.8, due to large pore diameters (Fig. 5, c). On the other hand, the TEOS/PhTES/CTAB particles (Fig. 5, a) attained very low values for the surface area and the pore volume, due to the presence of phenyl groups. Aromatic groups have planar configuration and large volume, which often confer rigidity and compactness to materials.

3.5. Bactericidal efficacy of microparticles in wastewater supernatants

In this research, the bacteriological activity of QAS-modified organosilica microparticles was explored against the common Gram-negative bacteria (E. ColiO157 and total Coliforms) by using the membrane filtration method. The results obtained for the bacteriological tests according to the methods described in the Experimental part are shown in Table 3.

Table 3

Bacteriological indicators for QAS-microparticles after 24 h contact with WW source

Indicator	WW source[*] control	TEOS/PhTES/ CTAB	TEOS/VTES/ CTAB	TEOS/VTES/ VBTAC	TEOS/-/ CTAB
E coli O157, CFU/100 ml	1	No modification compared to the control			>10
Total Coliforms, CFU/100 ml	39	No modification compared to the control			

[*] the volume of wastewater was 100 mL/ 0.5 g of microparticles

It can be noted that all the organosilica samples exhibited an interesting effect, with no modification against Coliforms. This behavior was clearly influenced by the presence of QAS-based stabilizers. When tested against E. ColiO157, the number of green spots cells have grown on the modified surfaces of TEOS/-/CTAB microparticles after 24 h of contact (Fig. 6a), in which case the low amounts of CTAB remaining after washing (as observed from FTIR) was the obvious cause. Nevertheless, all the other three systems with CTAB (Fig. 6b-TEOS/VTES/CTAB) and VBTAC (Fig. 6c-TEOS/VTES/VBTAC) have presented again no modification. These analyses have proved that the systems are indeed bacteriostatic, meaning the microparticles prevent the multiplication of microorganisms and decrease their vitality, without killing them.

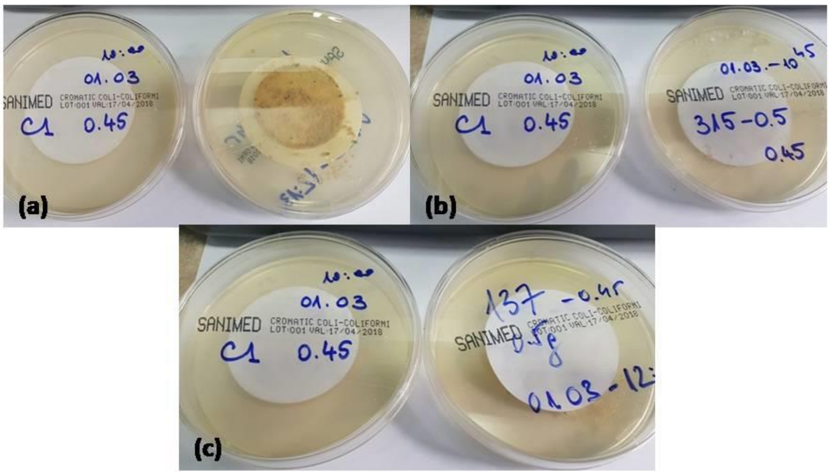

Fig. 6. Bactericidal performance of (a) TEOS/-/CTAB (b) TEOS/VTES/CTAB (c) TEOS/VTES/VBTAC organosilica microparticles against *E. ColiO157*

4. Conclusions

Two facile and easily controlled synthesis routes via sol-gel derived methods were described to prepare organosilica microparticles modified with QAS groups with bacteriostatic effect. The obtained QAS-organosilica microparticles were characterized by Scanning Electron Microscopy (SEM) and Dynamic light scattering (DLS) measurements in order to underline the morphology of interfaces and the mean particle size of the microparticles. The prepared particles were also analysed structurally and thermally. In order to assess the role of QAS load in the microparticles, the efficacy of microparticles was evaluated using wastewaters, containing Gram-negative bacteria (GNB), collected from a contaminated source. QAS-containing vinyl as well as phenyl (triethoxy silane) derived interfaces surprisingly exhibit bacteriological inert activity against E. Coli O157 and total Coliform bacteria for 24 h, demonstrating their potential value as a new generation of inert polymers used for bacteriological assays and even medical applications.

Acknowledgments

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