

Organic/inorganic hybrid nanospheres based on hyperbranched poly(ethylene imine) encapsulated into silica for the sorption of toxic metal ions and polycyclic aromatic hydrocarbons from water

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ABSTRACT

Organic–inorganic hybrid silica nanospheres were prepared through a biomimetic silicification process in water at ambient conditions by the interaction of low cost poly(ethylene imine) hyperbranched polymer with silicic acid. The characterization of these nanoparticles by FTIR spectroscopy, scanning electron microscopy (SEM), zeta-potential and dynamic light scattering (DLS) experiments confirmed that the dendritic polymer was incorporated into the silica network. Preliminary experiments show that these hybrid nanoparticles can be employed for the removal of toxic water contaminants. Hybrid nanospheres' sorption of two completely different categories of pollutants, i.e. metal ions such as Pb^{2+} , Cd^{2+} , Hg^{2+} , $Cr_2O_7^{2-}$, and polycyclic aromatic hydrocarbons such as pyrene and phenanthrene, was largely enhanced in comparison with the corresponding polymer-free silica nanospheres. This was attributed to the to the formation of conventional metal–ligand and charge–transfer complexes proving that although integrated into the silica network poly(ethylene imine) retains its chemical properties.

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1. Introduction

It is well known that amine-terminated dendrimers, as for example the commercially available poly(amidoamine) and poly(propylene imine) dendrimers, can encapsulate organic molecules [1] as well as metal ions dissolved in water [2–8] and can therefore be employed in water purification devices. Their properties depend on the structural characteristics of the branches in their interior, and on the large number of surface end-groups that are susceptible to functionalization or even multi-functionalization, affording polymers with diversified, tailor-made, properties so as, for instance, to render these polymers insoluble in water by attaching hydrophobic groups [9] or by performing cross-linking reactions [10].

In addition to dendrimers, hyperbranched polymers, their low-cost non-symmetrical analogues such as hyperbranched poly(ethylene imine) have also been shown to efficiently entrap heavy metal ions [11] and organic molecules in their interior and have been successfully employed for the removal of organic contaminants from water after appropriate functionalization in order to become insoluble in water [10–12].

These dendritic, i.e. dendrimeric and hyperbranched, polymers can either impregnate or be chemically attached on silica or ceramic membranes in general in order to develop hybrid organic/inorganic modules that can be easily installed in pre-existing filter units for water treatment [12–15]. However, the chemical modification with lipophilic or cross-linking groups, the chemical anchoring onto the ceramic surface, and the impregnation of the ceramic filters necessitate the use of harsh, toxic, energy consuming and not environmental-friendly chemicals, solvents and conditions. Thus, if these composite materials are to be employed in large-scale water remediation plants two profound necessities arise: The development of a production technique for these hybrid materials that has a lower cost and that employs, as much as possible, non-toxic chemicals, is not energy demanding and thus can be considered as an environmentally friendly process.

It has been recently established that biogenic silica is formed rapidly in water under mild conditions through a process known as biosilicification, which proceeds at ambient temperatures, pressures and pH values, producing an amazing diversity of nanostructure frameworks [16–18]. Examples of such biosilicification process are the diverse array of nanopatterned silica in many diatoms or the protective glass spicules of some sponges. It has been also shown that polycationic peptides called silafins [16], and the R5 peptide [19] isolated from diatom cell walls, generate networks of silica nanospheres within seconds when added to a solution of silicic acid. Further work conducted during the current decade has shown that a variety of homopeptides

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such as poly(arginine) and poly(lysine) [20], a combination of triethanolamine and cetyltrimethylammonium chloride [21] or amine-terminated dendrimers [22] can also act as biomimetic templates forming silica nanoparticles. Especially in the case of amine-terminated dendrimers, they can react in an amine concentration dependent fashion yielding silica nanospheres with a distinct size distribution. Additionally, the polymeric templates were encapsulated by the growing nanospheres and precipitated from water in a manner similar to that previously described for bioactive peptides.

Therefore, it was interesting to employ this method to obtain organic/inorganic hybrid materials avoiding the previously employed technique, i.e. functionalization by attaching hydrophobic groups or by performing cross-linking reactions, and finally impregnation into ceramic membranes. The integration of dendritic polymers in silica nanoparticles can be easily achieved under environmentally friendly conditions employing, as described above, a process mimicking biosilicification. Such nanomaterials could be suitable for water treatment provided that dendritic polymers, although incorporated in the nanospheres, retain their purification properties. A first indication that this is indeed feasible is given by a very recent study where an enzyme was encapsulated in a dendrimer silica nanocomposite [23]. It was shown that the enzyme, although trapped inside the mesoporous silica, was exhibiting mostly unchanged functionality.

It is therefore the scope of this study to initially investigate if the inexpensive but not perfectly symmetric, poly(ethylene imine) hyperbranched polymer (PEI) can form silica nanoparticles, if these particles are in the form of nanospheres, as those produced from their dendrimeric analogues. Finally, to investigate if PEI retains its chemical properties and specifically the ones related to the sorption of selected toxic compounds, and to explore the possibilities offered by these hybrid nanoparticles for water remediation. For this purpose the sorption properties of the composite materials obtained were tested towards two polycyclic aromatic hydrocarbons (PAH), i.e. pyrene and phenanthrene, and four selected toxic metal ions, specifically Pb^{2+} , Cd^{2+} , Hg^{2+} , and $\text{Cr}_2\text{O}_7^{2-}$.

2. Experimental

2.1. Materials and methods

Hyperbranched poly(ethylene imine), PEI, ($M_n = 5000$, 64–68 primary and secondary amino groups) was purchased from Hyperpolymers Inc. Pyrene (Aldrich) was purified by sublimation followed by recrystallization from ethanol. Phenanthrene, 4-(2-pyridylazo)-resorcinol (PAR) and tetramethyl orthosilicate were purchased from Aldrich, mercury(II) chloride, and lead (II) acetate trihydrate were purchased from Panreac, potassium dichromate was purchased from Riedel de Haën, cadmium sulphate 8/3 hydrate was purchased from Carlo Erba; all these compounds were used as received.

PAH concentration in water was determined by fluorescence spectroscopy, employing a Cary Eclipse Fluorescence Spectrophotometer after excitation at 333 nm for pyrene (emission 394 nm), and 248 nm for phenanthrene (emission at 364 nm). The concentration of solubilized inorganic ions was determined by UV-vis spectroscopy, employing a Cary 100 spectrophotometer. Specifically, the determination of Pb^{2+} , Cd^{2+} and Hg^{2+} was performed by measuring the absorption of the respective PAR complexes (PAR–Pb at 520 nm, PAR–Cd at 510 nm, PAR–Hg at 500 nm) employing a modification of the method proposed by Dagnall et al. [24]. Specifically, 0.1 ml of a buffer solution (ammonia–ammonium chloride pH 10) containing 10^{-2} M PAR were added to 2.9 ml of each water sample in 1 cm cuvettes and comparing the absorption with calibration

curves. The determination of $\text{Cr}_2\text{O}_7^{2-}$ was performed by measuring the absorption of the samples at 356 nm with the help of a calibration curve, determined employing standard solutions.

The presence of the hyperbranched poly(ethylene imine) in the silica particles and the formation of the siloxane bridges were established by FTIR spectroscopy employing a Nicolet Magna-IR Spectrometer 550. Thermogravimetry experiments were performed employing a TGA 2050 analyser (TA instruments). An AXIOS-150/EX (Triton Hellas) with a 30 mW He–Ne laser emitting at 658 nm and an Avalance detector at 90° was employed for size determination in typical dynamic light scattering (DLS) experiments. Zeta-potential measurements were performed employing a ZetaPlus (Brookhaven Instruments Corporation); the results represent the mean values of 10 zeta-potential measurements collected for each dispersion. X-ray diffraction experiments were performed using $\text{CuK}\alpha$ radiation from a Rigaku rotating anode X-ray generator (operating at 50 kV, 100 mA) and an R-AXIS IV image plate. Powder samples were sealed in Lindemann capillaries. The spherical shape of the nanoparticles was established by scanning electron microscopy using a JEOL 6380 LV instrument. N_2 -sorption experiments at -196°C were performed on an Autosorb-1 gas analyzer with Krypton upgrade (Quantachrome Corp.). Samples were out-gassed for 5 h at 120°C and 10^{-5} mbar vacuum. The surface areas were calculated according to the Brunauer–Emmett–Teller (BET) equation.

2.2. Preparation of silica nanoparticles

Sol–gel reactions were performed as described by Knecht et al. [25] for poly(amidoamine) and poly(propylene imine) dendrimers. In short, to 20 mM of phosphate buffer pH 7.5 a hyperbranched PEI solution of 10 ml (20 mM with respect to primary and secondary amine groups; for the calculation of amine group concentration an average number (65) of amino groups per hyperbranched macromolecule was used). To this solution was added 1 ml of 1 M silicic acid (prepared from the hydrolysis of tetramethyl orthosilicate in 1 mM HCl for 15 min at room temperature under stirring), upon which silica precipitation was instantaneous. The solutions were allowed to react while stirring for 5 min. Post-reaction, the assay mixture was centrifuged for 10 min ($12,000 \times g$), from which the supernatant was decanted, and the pellet was washed thoroughly with water (yield 77%). Silica precipitation could also be observed employing 2 mM PEI solution and 0.1 mM silicic acid. It should be noted that silica precipitation even occurred in the absence of phosphate buffer but to a much lesser yield (20%), while no silica precipitation was observed in phosphate buffer in the absence of PEI.

2.3. Determination of sorption kinetics

One hundred milliliters of metal or PAH solutions in ultra pure water (the concentration of all pollutants was 1 ppm except for pyrene which was 100 ppb purely because of its low solubility to water) were transferred into conical flasks. To these flasks 50 mg of PEI–silica or polymer-free silica nanoparticles were added. The pH of the PEI–silica and polymer-free silica solutions were 6.2 and 5.8 respectively. The resultant suspensions were continuously stirred and 5 ml samples were taken out at various time intervals and centrifuged. The concentration of the pollutant in the supernatant was determined spectrophotometrically as described above. The results reported are the average of two experiments.

2.4. Determination of sorption isotherms

Aqueous solutions (4 ml) of Hg^{2+} , Pb^{2+} and Cd^{2+} with concentrations $C_0 = 40, 70, 100, 150, 200, 300, 500, 1000 \text{ mg l}^{-1}$ were added

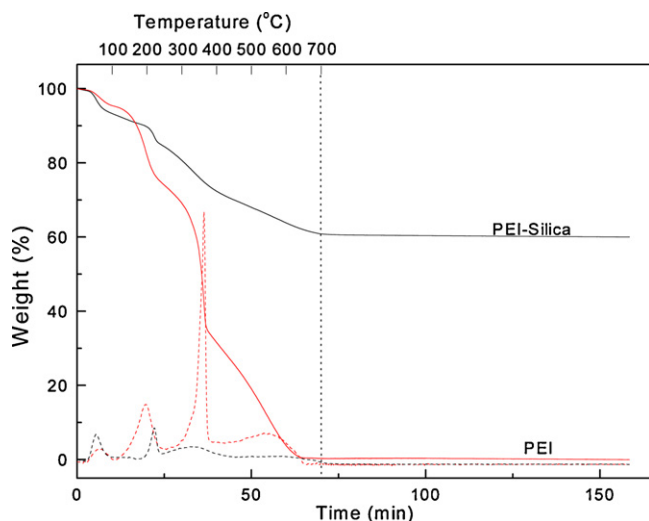


Fig. 1. Thermal decomposition profiles, and first derivatives thereof, of PEI and PEI-silica composite nanoparticles as a function of time and temperature.

to cylindrical flasks and 1 mg of PEI-silica or polymer-free silica nanoparticles was added in each flask. The flasks were placed in a shaker (Stuart Orbital Incubator S1500) at 25 °C and 200 rpm. After the sorption reached equilibrium (24 h), the equilibrium concentration, C_e , of each solution were determined as described above. The sorption amount at equilibrium, Q_e , was calculated according to

$$Q_e = \frac{V(C_o - C_e)}{m}$$

where V is the volume of the solution, m is the mass of the nanoparticles.

3. Results and discussion

3.1. Nanospheres' synthesis and characterization

The addition of metastable silicic acid into the PEI/phosphate buffer solution, pH 7.5, at room temperature caused immediate silica precipitation. In order to ensure that PEI co-precipitates, as observed in the case of the analogous symmetric dendrimers, thermogravimetry analysis was performed. Silica nanoparticles were heated at a rate of 10 °C/min up to 700 °C under airflow and then remained at that temperature for 3 h to ensure that constant weight is reached. As can be seen from the thermal decomposition profiles the composite particles lose about 40% of their initial weight while under the same conditions PEI is completely decomposed (Fig. 1). This weight loss, taking place primarily at higher temperatures, is indicating the presence of a large organic fraction in the material. Taken that the initial weight loss (up to ca. 100 °C) is due to moisture loss from silica; the silica/PEI molar ratio in the sample is calculated to be 1:150 which is very close to that reported by Knecht and Wright (137:1) [22] for the respective silica derived employing the fourth generation poly(propylene imine) dendrimer. This indicates the same silica formation mechanism, which is justified by the similar chemical structures of polymers compared. Furthermore, a comparison of the TGA curve of PEI with that of the composite nanoparticles reveals a different decomposition profile. This is a first indication of the existence of strong interaction between organic and inorganic moieties. Complete removal of organic traces was achieved with heating at 700 °C for 3 h. In this way "heat-treated" polymer-free silica nanoparticles were also produced and tested for comparison purposes.

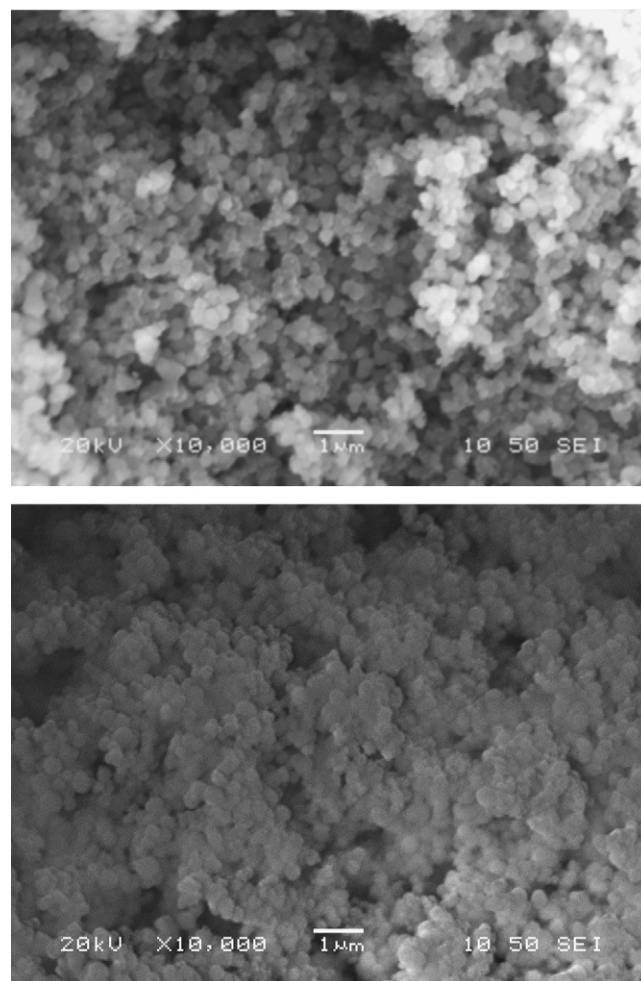


Fig. 2. SEM micrographs of spherical composite PEI-silica nanoparticles (upper part) and polymer-free silica nanoparticles (lower part).

Hybrid PEI-silica nanoparticles and polymer-free nanoparticles were observed employing scanning electron microscopy and both found to have spherical shape (Fig. 2). Particle size distribution of polymer-free and hybrid nanospheres was manually determined and found to be virtually the same. Respective mean diameters calculated (300 ± 69 and 305 ± 76 nm respectively) were in good agreement with the ones reported for the silica nanospheres produced employing poly(propylene imine) dendrimer possessing about the same number of terminal groups (258 ± 76 nm) [22]. Dynamic light scattering measurements of the nanospheres diameter in deionized water are considerably larger, i.e. 496 ± 73 and 470 ± 114 nm while respective diameters in 20 mM phosphate buffer are even larger, i.e. 622 ± 64 nm for the polymer-free and 768 ± 154 nm for the hybrid nanospheres. This observation could result from aggregation induced by charge neutralization due to the presence of phosphate buffer ions in the nanoparticles solvation sphere.

More specific information about the composite nanoparticles and their formation mechanism is attained employing infrared spectroscopy (FTIR). The spectra of PEI hyperbranched polymer, PEI-silica composite particles and polymer-free silica particles, i.e. silica particles without any organic material, are shown in Fig. 3 while the assignment of the FTIR bands observed is shown in Table 1. Silica absorption bands observed in both composite and polymer-free nanoparticles are typical to those of amorphous silica [26]. The amorphous nature of the obtained material was further confirmed by X-ray spectroscopy (data not shown). Most of the PEI

Table 1
FTIR frequencies (in cm^{-1}) and vibrational assignments of PEI, PEI–silica and polymer free silica particles.

Band assignment ^a	PEI	PEI (pH 7)	PEI–silica composite particles	Polymer free silica particles
ν_{as} NH	3350 (m)	3376 (br)	3370 (sh)	–
ν_s NH	3276 (m)	–	–	–
δ NH (overtone)	3188 (sh)	3260 (sh)	–	–
ν_{as} CH ₂	2932 (m)	2950 (m)	2962	–
ν_{as} CH ₂	2885 (m), 2807 (s)	2898 (m), 2831 (s)	2853	–
δ NH	1585 (m)	1602 (m)	–	–
δ_{as} NH ₃ ⁺	–	1500 (sh)	1524	–
δ_s NH ₃ ⁺	–	–	1473	–
δ CH ₂	1455 (s)	1455 (m)	1455	–
ν_{as} C–N	1105 (m)	1069 (m)	✓	–
ν_s C–N	1045 (m)	1017 (m)	✓	–
ν Si–O–Si	–	–	1042	1062
ν Si–OH, Si–O [–]	–	–	964	960
δ Si–O–Si	–	–	785	802
ρ CH ₂	760 (s)	761 (s)	✓	–
ρ Si–O–Si	–	–	442	450

^a Assignments: ν (stretch), δ (bend), ρ (rock). Subscripts *as* and *s* denote asymmetric and symmetric vibrations, respectively. Band intensities: *s* (strong), *m* (medium), *w* (weak), *sh* (shoulder); *br* (broad).

bands can hardly be detected in the hybrid PEI–silica particles' spectrum. The band of N–H asymmetric stretching is hardly observed at 3350 cm^{-1} while the symmetric and asymmetric stretching bands of CH₂ appear at 2962 and 2922 , 2853 cm^{-1} [27]. These bands are shifted to higher wavelengths compared to the same bands registered for PEI (2930 and 2285 , 2807 cm^{-1} respectively). This is justified taking into account the protonated character of the amine groups of PEI encapsulated in silica. In this connection, it should be noted that the corresponding vibration bands registered for PEI at pH 7, are also shifted towards higher wavelengths due to the partial protonation of the amine groups (cf. Fig. 3, column 2 in Table 1). The protonation of amine groups does not only affect the stretching mode of NH₂ groups as expected, but also the vibrational frequencies of the CH₂ groups that all are in alpha position relative to the (protonated) amine groups [28]. The same behavior is observed in the FTIR spectra of PEI–H₂SO₄ complexes [29]. Further proof of the protonated character of the NH₂ groups is obtained from the new bands observed in the PEI–silica nanoparticles at 1524 and 1473 cm^{-1} that are attributed to the symmetric and asymmetric bending modes of protonated NH₃⁺ groups. The stretching bands of C–N bonds (1100 – 1045 cm^{-1}) of PEI are overlaid by the broad Si–O–Si stretching band which, as a result, appears shifted at 1042 cm^{-1} in the PEI–silica nanoparticles compared to 1063 cm^{-1} in the spectrum of polymer-free silica. In a similar manner, the CH₂ rocking band at 760 cm^{-1} is under the Si–O–Si bending band (784 cm^{-1}) in the spectrum of PEI–silica while the band appears at 800 cm^{-1} in the spectrum of polymer-free silica.

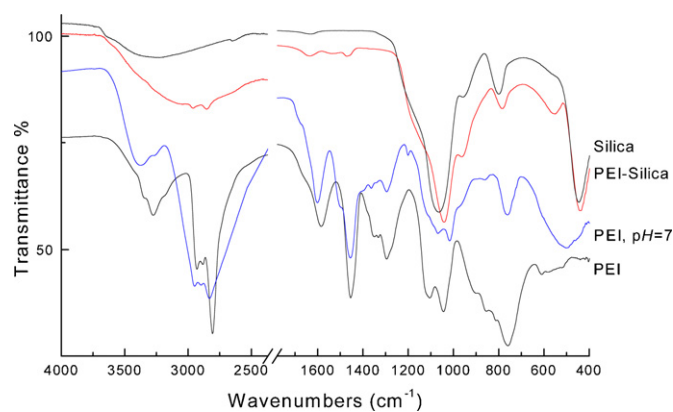


Fig. 3. FTIR spectra of hyperbranched poly(ethylene imine), PEI, organic–inorganic hybrid PEI–silica nanoparticles before (PEI–silica composite particles) and after thermal treatment for 3 h at $700\text{ }^\circ\text{C}$ (polymer-free silica particles).

As previously reported by Knecht and Wright [22] for poly(propylene imine) dendrimers, the amine groups of the unimolecular PEI hyperbranched polymer at pH 7 are partially protonated (in the form of NH₃⁺) and assume the traditional role of charge balance between the hyperbranched template and the surface of growing silica nanoparticles (Si–O[–] stretching band is present at 964 cm^{-1}). This consequently leads to the formation of an extensive network between NH₃⁺, Si–O[–] groups and water molecules that are evident in the spectrum of PEI–silica as a broad band centered at ca. 3000 cm^{-1} . Supporting evidences for the above can be also derived by comparing the pattern of the two spectra in the region 1750 – 1400 cm^{-1} . The 1473 cm^{-1} band has been attributed in previous studies to the symmetric bending mode of NH₃⁺ in the Si–O[–]...NH₃⁺ group [30,31] and the 1524 cm^{-1} band to the respective asymmetric bending of NH₃⁺ group. In addition, the medium to strong absorption band attributed to the bending of the NH₂ groups in the PEI spectrum at 1585 cm^{-1} is absent from the spectrum of the PEI–silica composite particles.

Porosimetry experiments (Fig. 4) revealed that the hybrid PEI–silica nanospheres are essentially non porous with a low BET surface area ($20.6\text{ m}^2/\text{g}$). The heat-treated polymer-free silica nanoparticles have an increased, due to the elimination of organic

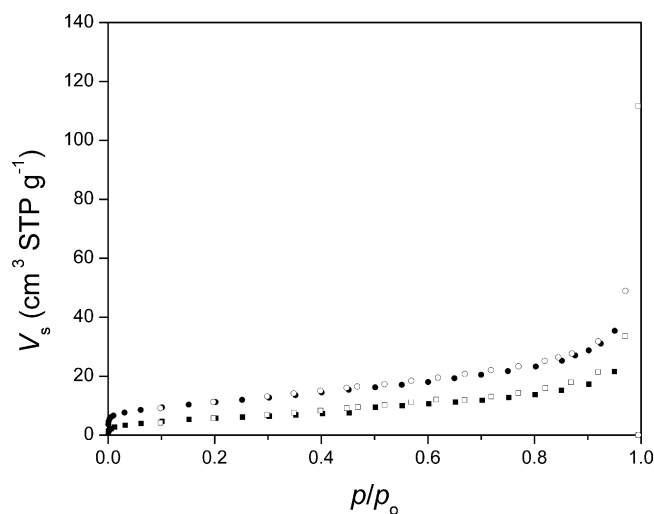


Fig. 4. N₂ sorption–desorption isotherms at $-196\text{ }^\circ\text{C}$ of hybrid PEI–silica nanoparticles (squares) and polymer-free silica nanoparticles (circles). Closed symbols: sorption, open symbols: desorption, V_s : N₂ sorbed volume, p/p_0 : relative pressure, STP: standard temperature and pressure.

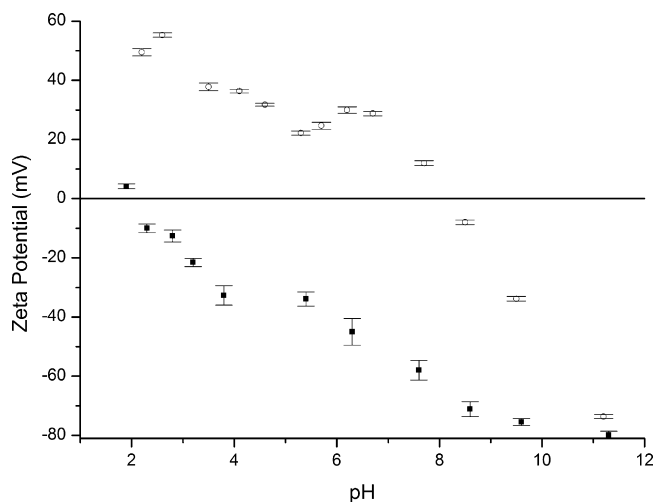


Fig. 5. Zeta-potential as a function of solution pH for Hybrid PEI-silica nanoparticles (open circles) and polymer-free nanoparticles (filled squares).

material, but still low BET surface area ($39.6 \text{ m}^2/\text{g}$). The pore size distribution in this case reveals pores with radii in the range of 2–5 nm.

Zeta-potential measurements were performed in water as a function of pH in order to determine the electrokinetic charge of the nanospheres, and the corresponding curves measured are shown in Fig. 5. The isoelectric point (IEP) of heat treated silica nanospheres is about 2, in accordance with what is typically observed for amorphous silica. Overall the nanospheres show a negative surface potential at low pH that decreases to about -80 mV at pH 11. The presence of PEI in the hybrid nanospheres should shift the IEP towards higher pH. Indeed, the hybrid organic-inorganic nanospheres have an IEP of about 8 that results from the presence of the protonated amino groups of the polymer. They have a positive surface potential of about $+50 \text{ mV}$ at pH 2 that decreases to about -70 mV at pH 11.

3.2. Sorption of heavy metal ions

3.2.1. Sorption kinetics

Silica by itself has been extensively studied as heavy metal ion sorbent from water [32,33]. The sorption has been described as a process governed by the electrostatic attractions between the positively charged metal ions and the negatively charged silica. Thus, heavy metal sorption rate into silica has been correlated to the ionic radius of the cation and the Z/R (charge/radius) ratio: Cations with bigger ionic radius create a smaller electric field and will be less likely to remain solvated in face to competition for complexation with the silanols. The larger radius also results in larger spread of electron configuration in space and greater tendency to polarize in response to the electric field of the negative charges the deprotonated silanols increasing the tendency to form complexes [34].

The presence of the negative charge at the polymer-free silica nanoparticles of the present work was confirmed by zeta-potential measurements. Heavy metal ion sorption percentages (Figs. 6 and 7) are consistent with the electrostatic nature of the driving force for the desolvation process. No sorption of the negatively charged $\text{Cr}_2\text{O}_7^{2-}$ into silica was observed and the sorption rate of the metal cations was almost analogous to their ionic radius [35] ($\text{Cd}^{2+} = 0.97 \text{ \AA}$, $\text{Hg}^{2+} = 1.1 \text{ \AA}$, $\text{Pb}^{2+} = 1.2 \text{ \AA}$; these values are referred for indicative purposes only), i.e. faster for the bigger lead ions and slower for the smaller cadmium ions. Nevertheless, after two days contact time no cation was detected in water.

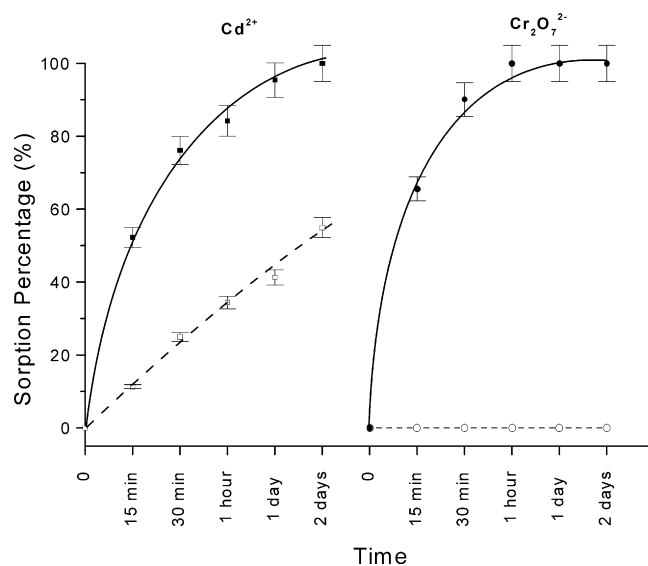


Fig. 6. Retention percentage of Pb^{2+} and Hg^{2+} from composite PEI-silica nanoparticles (solid curves) ($C_0 = 1 \text{ ppm}$, pH 6.2) and polymer-free silica nanoparticles (dashed curves) ($C_0 = 1 \text{ ppm}$, pH 5.4).

In contrast to the results reported for the polymer-free silica nanoparticles, $\text{Cr}_2\text{O}_7^{2-}$ sorption into hybrid PEI-silica nanoparticles is very fast (Fig. 6). No $\text{Cr}_2\text{O}_7^{2-}$ were detected spectrophotometrically after 1 h contact time with the above mentioned hybrid nanoparticles. $\text{Cr}_2\text{O}_7^{2-}$ sorption into supports functionalized with linear PEI due to PEI- $\text{Cr}_2\text{O}_7^{2-}$ complexation is well documented [36–38] and it is evident that these complexation properties are also exhibited by hyperbranched PEI although the latter is incorporated into the silica network. Combined with chelation, electrostatic interactions also play an important role allowing the anions to come close to the surface of the sorbing substrate. Hybrid nanoparticles examined by zeta-potential measurements were indeed found to be positively charged. Furthermore, the relatively high pH values did not seem to restrain sorption. Reported reduction of the Cr^{6+} to Cr^{3+} [37,38] by PEI was also identified from the green color of the Cr^{3+} species when the nanoparticles were dispersed in NaOH solutions. This is another evidence that

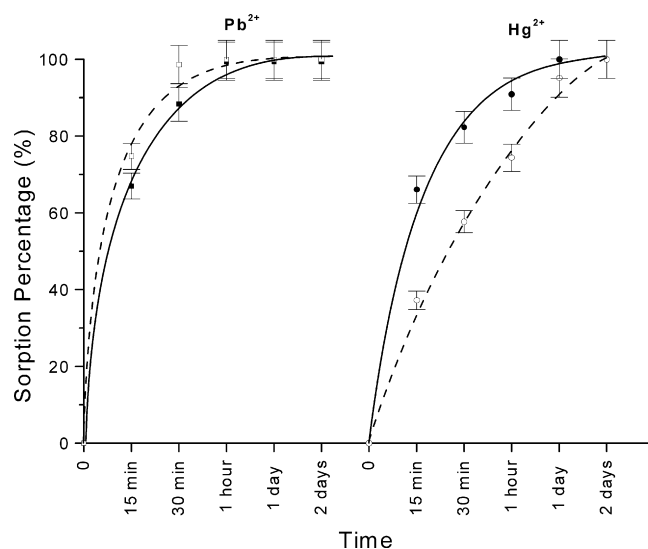


Fig. 7. Retention percentage of Cd^{2+} and $\text{Cr}_2\text{O}_7^{2-}$ from composite PEI-silica nanoparticles (solid curves) ($C_0 = 1 \text{ ppm}$, pH 6.2) and polymer-free silica nanoparticles (dashed curves) ($C_0 = 1 \text{ ppm}$, pH 5.4).

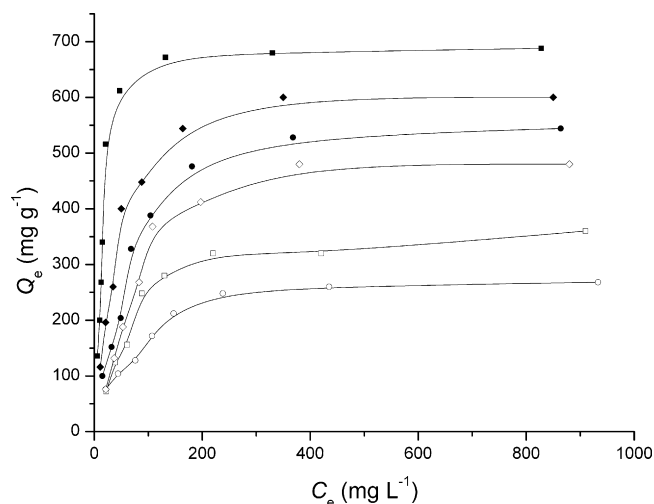


Fig. 8. Sorption isotherms for Hg^{2+} by hybrid PEI-silica nanoparticles (closed squares), Pb^{2+} by hybrid PEI-silica nanoparticles (closed diamonds), Cd^{2+} by hybrid PEI-silica nanoparticles (closed circles), Hg^{2+} by polymer-free silica nanoparticles (open squares), Pb^{2+} by polymer-free silica nanoparticles (open diamonds) and Cd^{2+} by polymer-free silica nanoparticles (open circles). Equilibration time = 24 h; Percent error = $\pm 5\%$.

the chemical properties of hyperbranched poly(ethylene imine) are also present in the hybrid nanospheres.

For the three other positively charged metal ions (Pb^{2+} , Cd^{2+} and Hg^{2+}) sorption into hybrid nanoparticles proceeds with a rate comparable (in the case of Pb^{2+}) or faster (in the cases of Cd^{2+} and Hg^{2+}) than polymer-free nanoparticles although unfavorable from the electrostatic point of view. Thus, PEI chelating properties, considered as the only factor responsible for the incorporation into hybrid nanoparticles, are sufficient not only to induce but also to enhance the sorption in comparison to the electrostatic interactions. The order of sorption rate $\text{Pb}^{2+} > \text{Hg}^{2+} > \text{Cd}^{2+}$ is the same with the sorption rate for the polymer-free nanoparticles and consistent with the lower chemical affinity of Cd^{2+} [39] and the strong chelating ability of PEI to Pb^{2+} [39] and Hg^{2+} [40]. Thus, in these cases too, PEI molecules surrounded by the siloxane network still retain their complex formation properties.

3.2.2. Sorption isotherms

The sorption isotherms of metal ions (Pb^{2+} , Hg^{2+} , Cd^{2+}) by the composite PEI-silica nanoparticles and polymer-free silica nanoparticles are shown in Fig. 8. Metal ion sorption can be approximated by a Langmuir type sorption isotherm model:

$$Q_e = \frac{Q_{\max} k C_e}{(1 + k C_e)}$$

where k = Langmuir equilibrium constant, C_e = metal concentration at equilibrium, Q_e = sorption amount at equilibrium, and Q_{\max} = maximum amount sorbed as C increases. The data of Figs. 8 and 9 were regressed linearly according to

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{k Q_{\max}}$$

and the results are presented in Fig. 9. From the slopes, $b = 1/Q_{\max}$, and the intercepts, $a = 1/(k Q_{\max})$, of the straight lines the k and Q_{\max} parameters are calculated (Table 2). These results indicate that the adsorption of all metal ions follow Langmuir-type adsorption mechanism yielding correlation coefficients R in the range (0.994–0.999). Composite PEI-silica nanoparticles exhibit greater affinity for the metal ions than polymer-free silica nanoparticles as was observed in the kinetic experiments. Polymer free silica nanoparticles exhibit the following adsorption capacity sequence expressed in mmole/g:

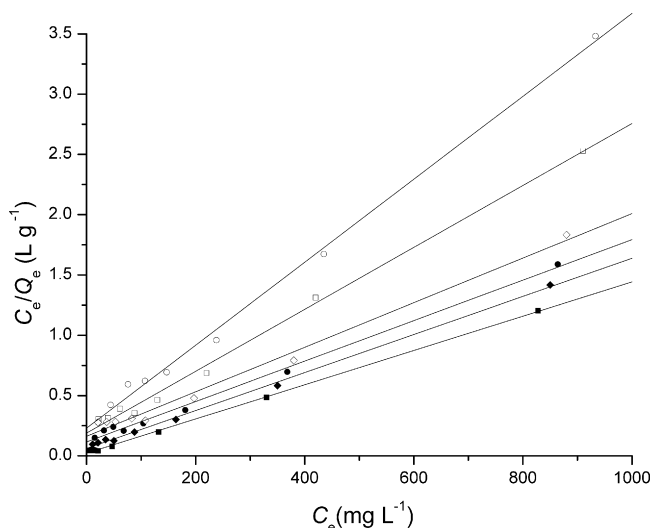


Fig. 9. Langmuir linear regression of the sorption isotherms of Hg^{2+} (squares), Pb^{2+} (diamonds) and Cd^{2+} (circles) ions by composite PEI-silica nanoparticles (closed symbols) and polymer-free silica nanoparticles (open symbols).

$\text{Hg}^{2+} < \text{Cd}^{2+} < \text{Pb}^{2+}$, whereas the respective order of hybrid PEI-silica nanospheres is $\text{Pb}^{2+} < \text{Hg}^{2+} < \text{Cd}^{2+}$. The smaller adsorption capacity of Pb is probably attributed to stereochemical reasons due to its larger size.

3.3. Sorption of polycyclic aromatic hydrocarbons

The sorption of polycyclic aromatic hydrocarbons into polymer impregnated ceramic membranes made from TiO_2 , SiC and Al_2O_3 has been previously reported employing continuous filtration experiments [10,14,15]. From the data presented in Fig. 10 it is evident that pyrene is sorbed by the polymer-free silica nanoparticles, in static sorption experiments down to a level of 40 ppb. On the other hand the sorption of the ten-fold more soluble phenanthrene is less favorable and 600 ppb remained after three days treatment with the silica nanoparticles.

However the presence of PEI into the silica nanospheres enhanced the sorption to a level of 12 ppb for pyrene and 230 ppb for phenanthrene. Polycyclic aromatic hydrocarbons are solubilized inside the nanoparticles in first place since they are practically insoluble in water and they are, therefore, at a high-energy state. Thus, their inclusion in the environment of these nanospheres is a thermodynamically favorable process [12]. Secondly, the solubilization into the hybrid nanoparticles is further amplified by the formation of charge-transfer complexes between polyaromatics

Table 2
Sorption parameters for Langmuir model.

	R	Q_{\max}	k
Hg-silica-PEI	0.9996	704.22 mg/g 3.511 mmol/g	0.065 l/mg 13.017 l/mmol
Hg-silica	0.9977	389.11 mg/g 1.940 mmol/g	0.014 l/mg 2.741 l/mol
Pb-silica-PEI	0.9992	632.91 mg/g 3.055 mmol/g	0.026 l/mg 5.404 l/mmol
Pb-silica	0.9944	540.54 mg/g 2.609 mmol/g	0.011 l/mg 2.371 l/mol
Cd-silica-PEI	0.99759	595.24 mg/g 5.295 mmol/g	0.015 l/mg 1.640 l/mmol
Cd-silica	0.9982	290.70 mg/g 2.586 mmol/g	0.015 l/mg 1.683 l/mol

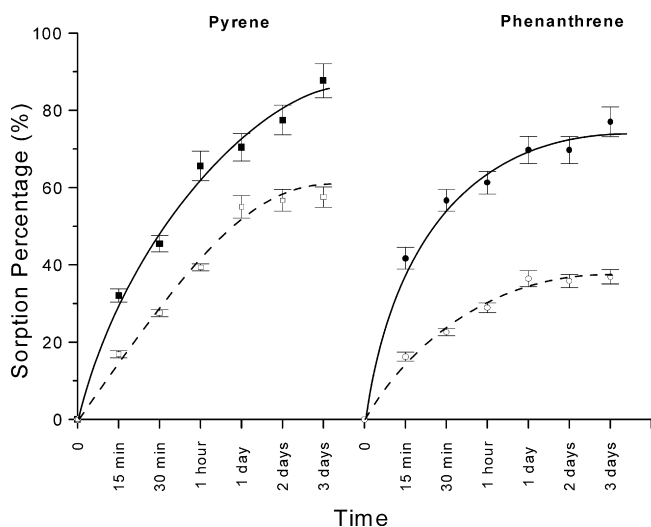


Fig. 10. Retention percentage of polycyclic aromatic hydrocarbons from composite PEI-silica nanoparticles (solid curves) and polymer-free silica nanoparticles (dashed curves) ($C_{0,\text{pyrene}} = 100$ ppb, $C_{0,\text{phenanthrene}} = 1$ ppm).

and the tertiary amino groups of the hyperbranched polymer [41]. As a result PEI-silica nanoparticles present a promising alternative to hybrid organic/inorganic filter modules for PAH sorption from water.

3.4. Ecological benefits

A comparison of the preparation process (see also Section 2) with previous techniques reveals its ecological advantages. The biomimetic synthesis reaction which takes place in water at ambient conditions in a one step reaction realizes three purposes: (a) the manufacturing of the ceramic material (b) the functionalization of the hyperbranched polymer, rendering it insoluble in water and (c) the binding of the hyperbranched polymer to the ceramic. Silica preparation by the classical sol-gel method is a time but most of all energy consuming process and requiring elevated temperatures. Functionalization of the hyperbranched polymer and binding to the ceramic material takes place in toxic organic solvents such as chloroform, acetonitrile and methanol while, additionally binding requires heat. It is thus obvious that by implementing the above described method energy consumption will be spared and considerable quantities of toxic wastes and volatile carbon emissions will be avoided.

4. Conclusions

The biomimetic synthesis of hybrid silica/dendrimeric polymer nanoparticles can also be performed with the less expensive non-symmetric hyperbranched poly(ethylene imine), affording spherical particles. Sorption experiments indicated that these nanospheres have a tendency to remove toxic substances from water such as polycyclic aromatic hydrocarbons and heavy metal ions. The characterization of these materials led to the conclusion that this sorption is attributed to electrostatic interactions and is further enhanced either due to the chelation properties of the hyperbranched polymer towards the metal ions or due to the formation of a charge-transfer complex between polycyclic aromatic hydrocarbons and tertiary amino groups, proving that, although incorporated into the silica network, poly(ethylene imine) retains its chemical properties. The method that has been described for the preparation of hybrid PEI-silica nanospheres under mild environmental friendly conditions presents an interesting alternative to the conventional methods of the chemical attachment of

dendritic polymers on ceramics or the manufacturing of hybrid organic/inorganic ceramics by impregnation with the dendritic polymer. The nanospheres obtained have the potential for pollutant encapsulation and water remediation.

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