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Synthesis of organic–inorganic hybrids via adsorption of dye on an aminosilane-functionalised silica surface

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Abstract

Studies were performed on synthesis of a monodisperse active silica in an emulsion system. The obtained silica was subjected to surface modification using *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane in order to increase the chemical (mainly adsorptive) reactivity of the silica. On the surfaces of the raw silica material and the aminosilane-functionalised silica C.I. Reactive Blue 19 was adsorbed. The ensuing silicas and pigments were subjected to physicochemical evaluation using spectrophotometric, microscopic and laser light scattering techniques; also the specific surface area and pore characteristics were determined. Amounts of the adsorbed silane and dye were determined employing elementary analysis; the amount of silane and of dye both adsorbed and eluted from the surface of SiO_2 were estimated. The silicas and pigments exhibited an almost ideal spherical particle shape and a highly uniform character of particles. This was particularly evident following adsorption of C.I. Reactive Blue 19 dye on the surface of aminosilane-modified silica. The dye was found to have chemically reacted with the aminosilane-grafted silica surface, which was proven by FTIR spectra and elementary analysis. The character was also confirmed by an alteration in value of the isoelectric point. Silicas formed in the emulsion system were found to represent a highly valuable adsorptive material, which might serve as a dye carrier. Pigments obtained in this way are chemically and physically stable.

Keywords: Spherical silica; Emulsion precipitation system; Surface modification; Adsorption of dye

1. Introduction

The adsorptive properties of silicas make them very attractive research and technological materials [1,2]. The presence of surface, functional silanol and siloxane groups, and their reciprocal ratio, characterise chemically active or chemically passive surfaces [1,3–5]. In the physical sense, their adsorptive character is determined mainly by their specific surface area, size and volume of pores. Such traits of silicas may be determined by selection of the method in which the silicas are manufactured. Depending on their formation, they may assume the role of a typically physical adsorbent or, due to the introduction of appropriate organic groups, of a chemical adsorbent.

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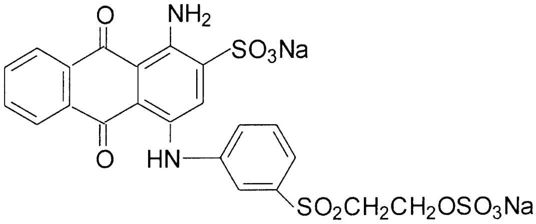
Various mechanisms may account for the interaction of a dye with modified silica surface. For instance, the silica staining process includes an initial reaction of silica with a silane coupling agent, to which, the dye then binds. In such a situation, SiO_2 particles carry on their surface a dye that is covalently bound [6–9] to the silane coupling agent and cannot be washed off with solvent, so reducing the toxicity of, e.g., components of a printer's ink. Silica-based colour pigments may also be obtained using three- or four-stage procedures. The technique can be used for various types of silica, dyes and organic pigments [10]. The formation of pigments directly during the course of silica synthesis utilises, as a carrier, the silica obtained in the course of tetraethoxysilane (TEOS) hydrolysis and condensation reaction in ethanol/water/ammonia mixture (the so-called Stöber's technique of silica formation [11]) and in presence of cationic dyes such as, e.g. C.I. Basic Blue 9 [12,13].

This work aimed at obtaining optimum silica carrier (adsorbent) of a defined shape and particle size. Such a silica should also carry a chemically reactive surface obtained in the course of the suggested synthesis. It was decided to prepare the silica in an emulsion system. Additionally, an attempt was made to intensify the interaction of the silica carrier with dye by silica surface modification using a silane coupling agent. In the subsequent part of the study, adsorption was performed and the physicochemical properties of the surfaces were established for the precipitated modified and unmodified silicas as well as for the ensuing pigment.

2. Experimental

2.1. Materials

Newly synthetised silica was used, precipitated in an emulsion medium from sodium metasilicate and hydrochloric acid solution. For the silica surface modification *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (UniSil) was used. Colouration of silica was conducted using C.I. Reactive Blue 19 (Boruta-Kolor) of the following structure:



2.2. Procedures and methods

The reaction of silica synthesis was preceded by preparation of two emulsions. The emulsion (A) contained an aqueous solution of sodium metasilicate and cyclohexane while the emulsion (B) consisted of hydrochloric acid and cyclohexane. In both emulsions a non-ionic, surfactant (oxyethylenated unsaturated fatty alcohol of general formula: $RO(CH_2CH_2O)H$, $R = C_{16-22}$, $n \cong 7$) was obtained from ROKITA, S.A. The emulsions were prepared employing a homogeniser (19,000 rpm).

The process of silica precipitation was conducted in a reactor of 5 dm^3 capacity, charged with the emulsion (B). Emulsion (A) were dosed at a constant rate, mixing the reaction system by the use of a ULTRA TURRAX T50 Basic homogeniser (IKA Labortechnik; 10,000 rpm). The reaction was conducted at room temperature and the formed silica yielded the third emulsion which was heated to 80 °C and the hot mixture distilled to remove the organic phase. The remaining silica was filtered and the filter cake placed in a stationary drier at 105 °C for 48 h.

Surface modification of the silica obtained from the emulsion system was performed using *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (3 parts by mass of SiO_2), pre-hydrolysed in a methanol/water, 4:1, v/v solution prepared directly before modification in order to avoid ageing effects. The modification was performed in a specially designed reactor [14] over course of 1 h and the solvent was distilled off.

Adsorption of C.I. Reactive Blue 19 on the silica surface which had been modified with 3 parts of aminosilane or on the unmodified silica was carried out by introducing a solution of the dye (2 mg/cm^3) to the silica-containing reactor. Formation of the inorganic–organic hybrid was performed in 30 min under intense mixing (10,000 rpm). The obtained product was filtered and the remaining filtrate displayed an absorbance (SECOMAN S750 spectrophotometer) which showed dye adsorption both on the unmodified and on the modified silica.

The morphology and surface structure of the unmodified and the modified silica carrier and also the obtained pigment were examined using a Jeol 1200 EX II transmission electron microscope.

The particle size was measured using a ZetaPlus apparatus (Brookhaven) by dynamic light scattering. Particle distribution in the size distribution curves was used to determine polydispersity as a measure of homogeneity of the silica colloids.

The specific surface areas of the silica powders were determined by N_2 adsorption (BET method) using a Micrometrics ASAP 2010 instrument; the volume and size of the pores of the precipitated materials were also examined. Samples were degassed at 120 °C for 2 h prior to measurements.

The relation between zeta potential and pH (determination of isoelectric point) was determined using the ZetaPlus apparatus by direct measurement of electrophoretic mobility; ionic strength was adjusted to 10^{-3} mol/dm^3 using NaCl solution.

The extent of modification and the character of the reaction between silane coupling agent, dye and the silica were established using Bruker FTIR EQUINOX equipment employing KBr tablets.

The raw silica material and functionalised silica samples were characterised by quantitative elemental analysis (C, H, N and S analysis) using a Carlo-Erba EA 1108 instrument.

3. Results and discussion

The raw silica material (Sample 1) obtained in the emulsion system manifested high bulk density (283 g/dm^3) and a high capacity to absorb water (250 cm^3/100 g); the capacities to absorb paraffin oil and dibutyl phthalate were relatively low (300 cm^3/100 g and 200 cm^3/100 g, respectively). The silica grafted by *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (Sample 2) exhibited a slightly lower bulk density (261 g/dm^3) and a slightly lower capacity to absorb water (200 cm^3/100 g). On the other hand, the silica capacities to absorb paraffin oil and dibutyl phthalate showed insignificant increases (to 350 cm^3/100 g and 250 cm^3/100 g, respectively). The adsorption of C.I. Reactive Blue 19 on the surface of the modified silica (Sample 3) imparted no significant changes. The principal physicochemical parameters for the pigment were as follows: bulk density: 234 g/dm^3, water-absorbing capacity: 200 cm^3/100 g, capacity to absorb paraffin oil: 350 cm^3/100 g, capacity to absorb dibutyl phthalate: 250 cm^3/100 g. The reference sample (Sample 4) or the product of the dye adsorption on the unmodified silica carrier exhibited the lowest bulk density (210 g/dm^3) of all of the products. Its water-absorbing capacity was slightly lower than the corresponding capacity of the raw silica (200 cm^3/100 g) while its capacities to absorb paraffin oil and dibutyl phthalate remained unchanged.

Particle size distribution and electron-microphotograph of the unmodified silica are presented in Fig. 1a and 1b, respectively. The mean particle diameter was 792.0 nm and polydispersity was 0.059, the latter value proving that the silica particles were highly uniform. In the particle size distribution (Fig. 1a) two bands are visible. The more intense band reflects the presence of silica particles of lower diameter and fitted the range 391.6–684.6 nm (maximum intensity of 100 corresponded to the particle diameter of 489.6 nm). The band in the range of 3658.7–5.905.8 nm reflects the presence of particles of much higher diameter and also of particle aggregates; it was of lower intensity (maximum intensity of 5 corresponded to particles of a diameter in the range of 4431.0–5366.4 nm). Transmission electron-microscopy (TEM) (Fig.1b) confirmed the presence of almost spherical particles of small diameters. Some of the particles formed large accumulations (so called agglomerates), which represented an undesirable effect.

The particle size distribution and TEM microphotograph of a silica modified with 3 parts of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane are presented in Fig. 2. Mean particle diameter in the silica was 507.3 nm while its polydispersity value was as low as 0.005. This indicated a most advantageous effect of the aminosilane on silica dispersion. In the particle size distribution (Fig. 2a) two bands were seen, related to presence of particles of low and of much higher diameters, respectively. The more intense band was linked to the presence of particles of lower diameters, in the range of 315.9–71.6 nm (maximum intensity of 100 corresponded to particles of 370.8 nm in diameter). Silica modified with 3 parts of aminosilane manifested the presence of particles of lower diameter as compared to the unmodified silica. The band in the range of 2104.6–2571.3 nm, reflected the presence of larger particles and of agglomerates and was of lower intensity (maximum intensity of

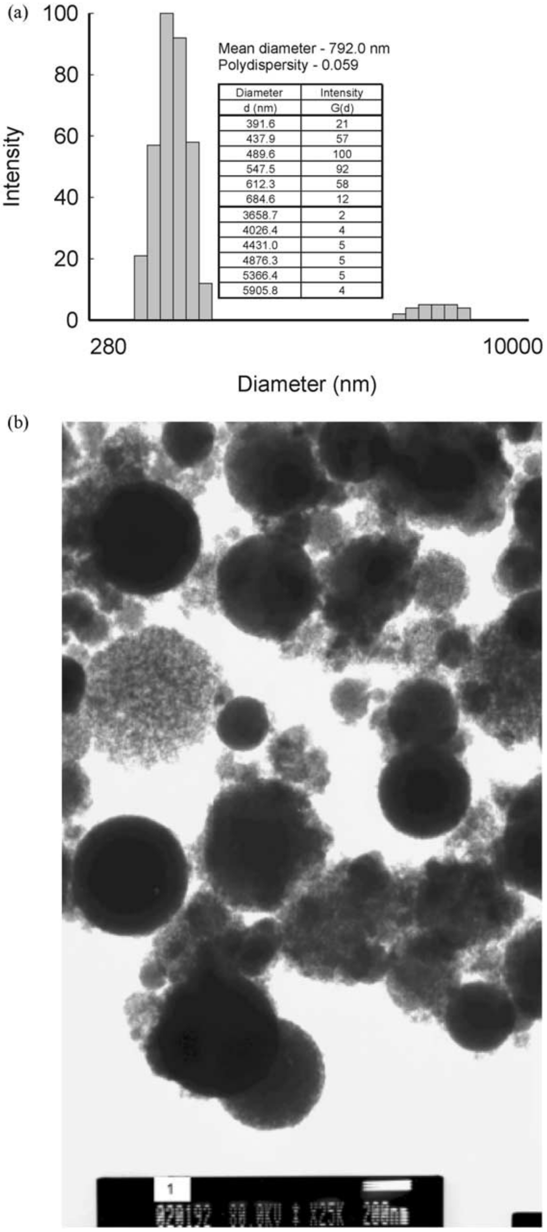


Fig. 1. (a) Multimodal particle size distribution and (b) transmission electron micrograph (TEM) of raw silica material.

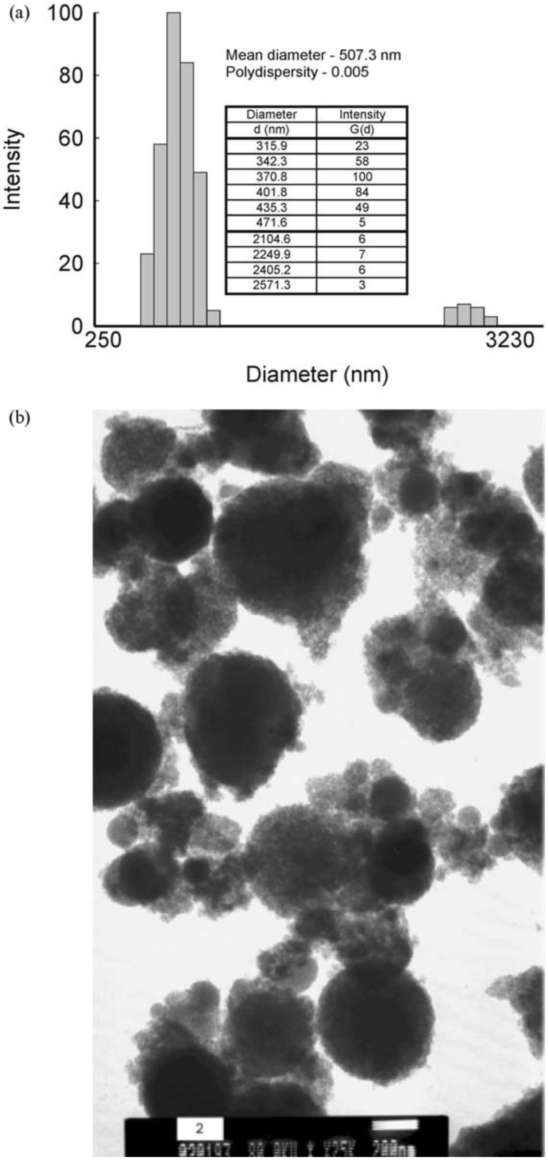
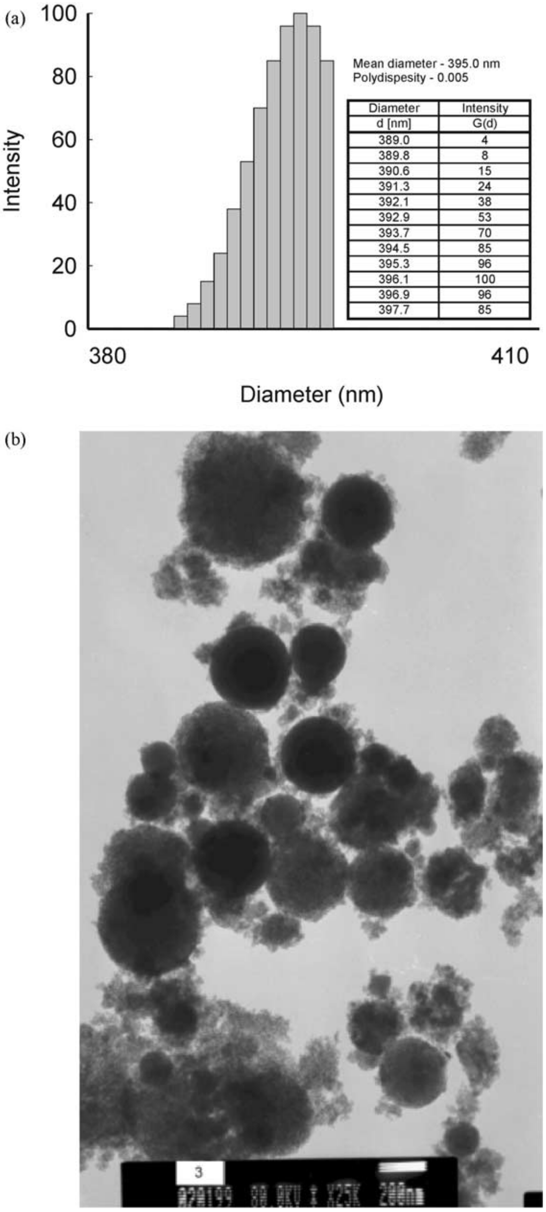


Fig. 2. (a) Multimodal particle size distribution and (b) transmission electron micrograph (TEM) of aminosilane-functionalised silica.

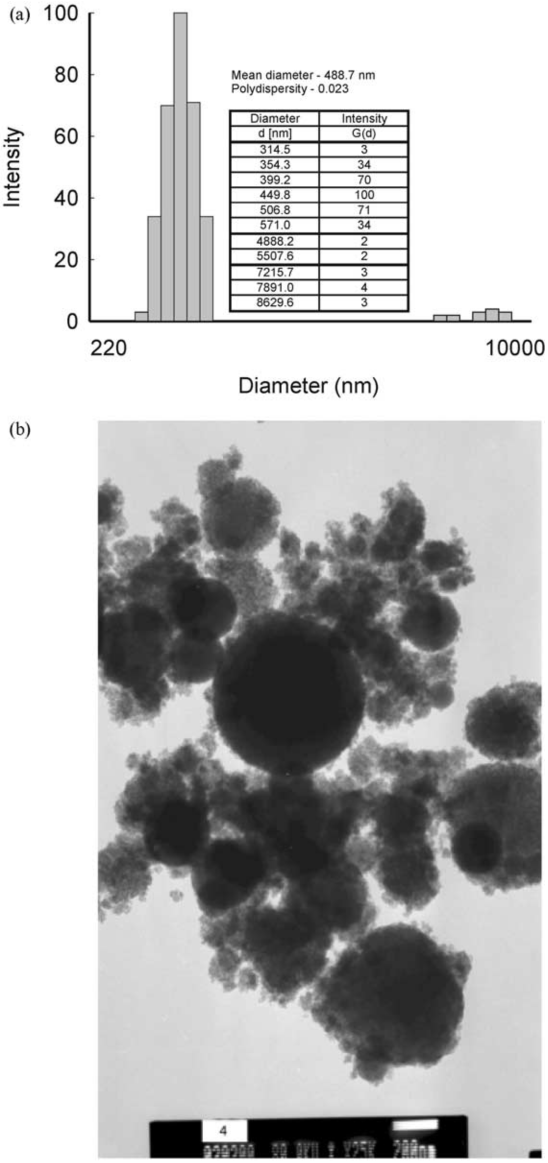
7 corresponded to the particle diameter of 2249.9 nm). The spherical shape of the particles is shown in Fig. 2b and indicates that the modified silica was highly uniform. Silica particles were present in the form of much smaller, spherical grains.

Adsorption of C.I. Reactive Blue 19 on the silane-functionalised silica surface markedly reduced particle diameter (to 395.0 nm). Moreover, the silica was highly uniform, with a polydispersity of 0.005. In the particle distribution curve (Fig. 3a) only one band was present, in the



Diameter d [nm]	Intensity G(d)
389.0	4
389.8	8
390.6	15
391.3	24
392.1	38
392.9	53
393.7	70
394.5	85
395.3	96
396.1	100
396.9	96
397.7	85

Fig. 3. (a) Multimodal particle size distribution and (b) transmission electron micrograph (TEM) of a dye adsorbed on the aminosilane-functionalised silica surface.



Diameter d [nm]	Intensity G(d)
314.5	3
354.3	34
399.2	70
449.8	100
506.8	71
571.0	34
4888.2	2
5507.6	2
7215.7	3
7891.0	4
8629.6	3

Fig. 4. (a) Multimodal particle size distribution and (b) transmission electron micrograph (TEM) of a dye adsorbed on the unmodified silica surface.

diameter range of 389.0–397.7 nm; maximum intensity of 100 corresponded to the particle diameter of 396.1 nm. TEM (Fig. 3b) confirmed the presence of spherical and highly uniform particles.

A completely distinct dispersive and morphological character was illustrated by the data of Fig. 4 which shows silica which has been modified by coating its surface with the dye. The primary particles are accompanied by aggregate and agglomerate structures; such secondary, undesirable effects show that this pathway should be abandoned.

Apart from the chemical character of the surface, specific surface area represents the most sigificant determinant of the adsorption properties of the silica. The raw silica material displayed high specific surface area (182 m^2/g) and showed the highest total volume of pores (48 cm^3/g). Silica surface modification with aminosilane and subsequent dye adsorption blocked the inner pores to a significant extent which was reflected by a marked change in specific surface area. For sample 2 [functionalised by *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane] the specific surface area was 119 m^2/g and, following adsorption of C.I. Reactive Blue 19 on the modified silica (sample 3), the specific surface area reached a value of 96 m^2/g. Adsorption of the dye directly on the unmodified silica did not induce radical changes in surface development (Table 1).

Zeta potential provides information about the stability of dispersion and, indirectly, of chemical reaction of a modifier and, indirectly, of a dye with the silica surface.

The dependence of zeta potential on pH is presented in Fig. 5. For the unmodified silica the isoelectric point was, approximately, 1.7. The pronounced surface protonisation effect imparted

Table 1
Specific surface area, volume and average size of pores of obtained silicas

Sample No.	Specific surface area BET (m^2/g)	Total pores volume (cm^3/g)	Pores volume 17 to 30,000 Å (cm^3/g)		Average size of pores[a] (Å)
			From adsorption curve	From desorption curve	
1	182	0.45	0.4987	0.4996	99.24
2	119	0.34	0.3907	0.3913	114.16
3	96	0.27	0.3407	0.3411	112.00
4	174	0.36	0.4051	0.4058	96.91

[a] Calculated from BET equation (4V/A).

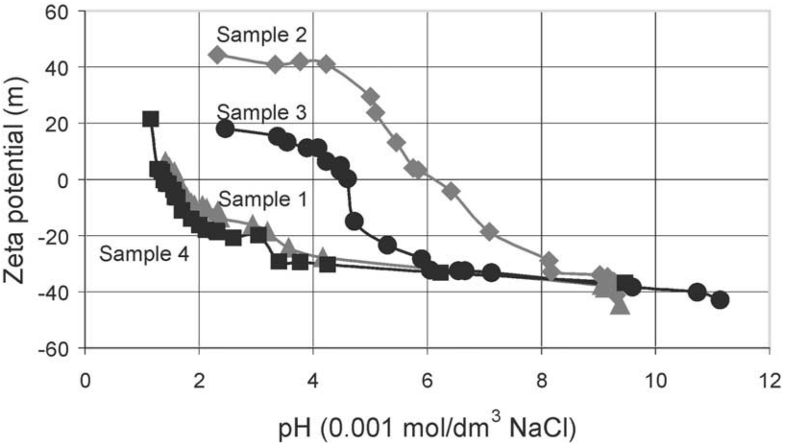


Fig. 5. Zeta potential as a function of pH for the investigated silicas.

by the *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane is clearly evident, as it significantly affected zeta potential and, therefore, the value of the isoelectric point (sample 2). In this case, the isoelectric point reached the value of, approximately, 6.1. Adsorption of the organic dye was followed by a change in isoelectric point in the acidic direction, to 4.8. All of the studied silicas used demonstrated a similar zeta potential, in the range of pH 8–12. In such cases, zeta potential demonstrated a negative charge. Extensive differences in the value of zeta potential, depending on the way in which the silica was processed, were seen in the region of $\mathrm{pH} < 7$. The highest stability was shown by aminosilane-modified silica at $\mathrm{pH} = 2$–4. In such situations, zeta potential showed values approaching −40 mV (Fig. 6).

FTIR revealed that silica obtained using the emulsion system as a reactive medium did not exhibit the surface chemistry typical of classically obtained hydrated silica. The band at 3750–3660 $\mathrm{cm^{-1}}$, typical for an isolated silanol group, geminal or vicinal groups was practically absent. This probably reflected the effects of the adsorbed surfactants that were used during emulsion preparation and during silica precipitation. In contrast, the intense band of 2965–2850 $\mathrm{cm^{-1}}$, indicated the presence of stretching C–H bonds. The intensity of the band increased following chemisorption of organic agents (silane and dye) on the surface of SiO_2. These findings were confirmed by elementary analysis of the studied silicas (Table 2).

In the case of the pigment obtained by the reaction of C.I. Reactive Blue 19 with the aminosilane-functionalised silica surface, adsorption was highly efficient (99.1%). This reflected formation of a stable chemical bond of the covalent type between the silane and the dye. The probable mechanism involved initial transformation of the 2-sulphatethylsulphonic ($SO_2CH_2CH_2OSO_3Na$) group into the vinylsulphone from

Table 2
Elementary analysis of the examined silicas

Sample No.	Contents (%)		
	C	N	S
1	10.21	0.00	0.00
2	14.75	0.35	0.00
3	15.81	0.54	0.15
4	10.41	0.10	0.00

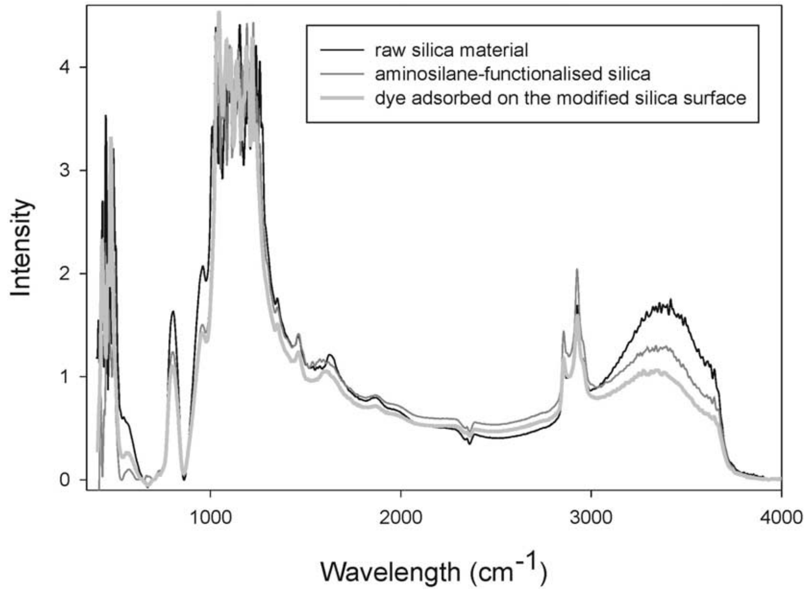
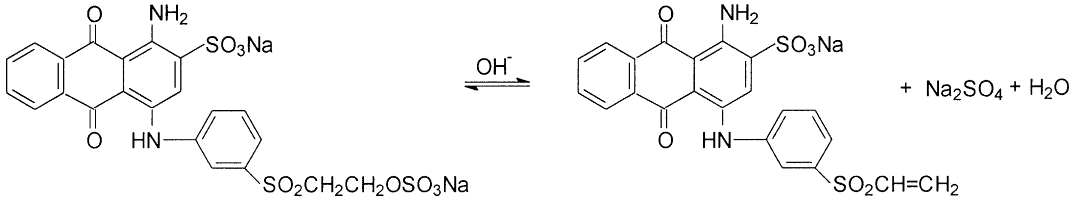


Fig. 6. FTIR spectra for the examined powders.

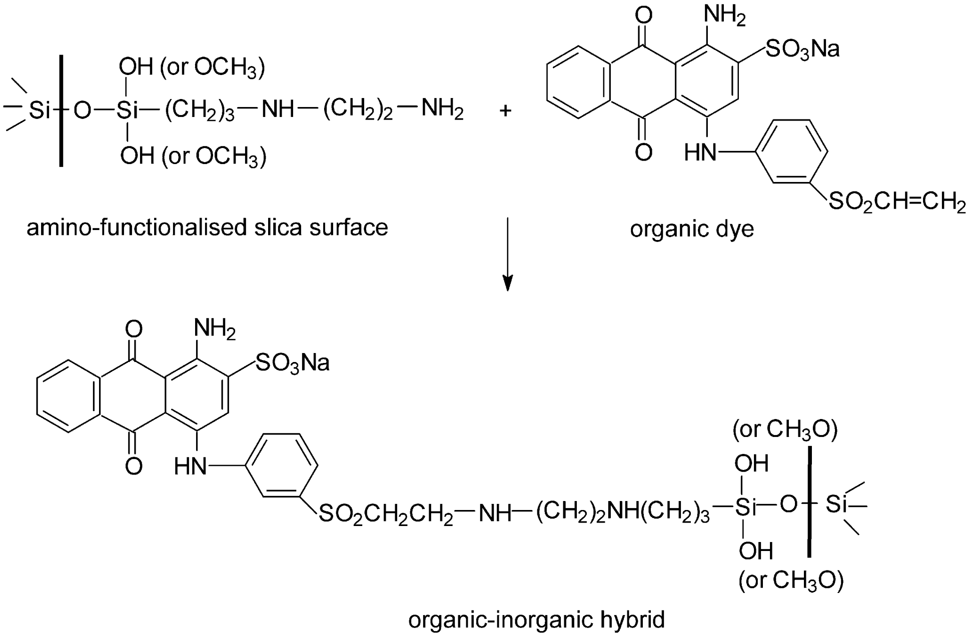
Table 3
Adsorption extent and amount of eluted dye of the investigated silicas

Sample No.	Dye concentration before adsorption (mg/cm^3)	Dye concentration after adsorption (mg/cm^3)	Disposal extent (%)	Dye concentration after elution (mg/cm^3)	Amount of dye eluted from silica surface (%)
3	2.000	0.019	99.05	0.050	10.10
4	2.000	0.450	77.50	0.057	14.71

($SO_2CH=CH_2$). Under alkaline conditions, the group split off sulphuric acid, as follows:



The formed vinylsulphone group, in turn, might then react with the modified carrier surface thus:



Interaction of the dye with the surface of the unmodified silica (precipitated in the special emulsion system) was mainly physical in nature. In such a case, the extent of adsorption was much lower and amounted to 77.5%. In general, the extent of adsorption depended on the chemical structure of silica surface used. However, the amount of dye extracted from the aminosilane-grafted silica surface and from the raw silica material was no longer high and was of the order 10.1 and 14.7%, respectively. This reflected the relatively high chemical reactivity of C.I. Reactive Blue 19 to the unmodified silica due to the hydrophobic transformation of the silica surface, reflecting introduction of multiple organic substances in the course of preparation in the emulsion system (Table 3).

4. Conclusions

The silica carrier, precipitated in the emulsion system, exhibited uniform particles that were of almost ideal spherical shape. An increase in particle homogeneity was noted in particular following adsorption C.I. Reactive Blue 19 on the amino-functionalised silica surface. Due to silica surface modification with aminosilane the reaction with the dye was chemical in nature, as confirmed by spectroscopic examination and by elementary analysis. Changes in the surface character could also be monitored due to protonising effects of the applied silane on zeta potential and, indirectly, on iso-electric point. The extent of dye adsorption on the modified SiO_2 surface exceeded that for the unmodified silica.

Acknowledgements

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