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Hybrid pigments preparation via adsorption of C.I. Mordant Red 3 on both unmodified and aminosilane–functionalised silica supports

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ABSTRACT

The adsorption of C.I. Mordant Red 3 on the surface of silica both unmodified and modified with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane was studied. The efficiency of C.I. Mordant Red 3 adsorption on silica and the adsorptive properties of inorganic support were characterised. The particle size distribution and the surface morphology of the pigments obtained were determined, their physico-chemical properties were characterised and the colorimetric analysis was performed. The degree of silica support coverage with the organic dye was estimated on the basis of elemental analysis. The presence of functional groups on silica and on the pigments was verified with the FT–IR analysis.

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1. Introduction

Typical supports for the adsorption of organic dyes are silica, titania, alumina, etc. [1–4]. As could be followed from earlier studies, the use of modified silica support in the dye adsorption processes leads to the obtaining pigments of smaller particles and to an increase efficiency of the dye adsorption. According to the colorimetric analysis the brightness of the pigments obtained depends on the type of modifier used. The organic dyes used in the aforementioned studies were C.I. Acid Red 18 and C.I. Acid Violet 1 and the silica support was modified with different silane coupling agents [5–8]. The adsorption of C.I. Basic Blue 9 or C.I. Basic Red 5 on silica obtained from the emulsion system was proved to occur with 99.9% efficiency. The pigments obtained were stable and characterised with a low degree of the dye elution from the support surface [9,10]. The adsorption of C.I. Reactive Blue 19 on the aminosilane–modified silica surface resulted to an increased uniformity of the pigment particles [11,12]. The pigments obtained by adsorption of C.I. Acid Orange 7 or C.I. Reactive Blue 19 on the surface of TiO_2 modified with aminosilane containing one or two $-NH_2$ groups were also studied. The presence of the functional groups on TiO_2 surface (after modification) resulted to an increased efficiency of adsorption of C.I. Acid Orange 7 and reduced dye elution from the support. The adsorption of C.I. Reactive Blue 19 on TiO_2 modified with 3-aminopropyltriethoxysilane caused an increase in the adsorption efficiency, whereas, on TiO_2 modified with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane led to its decrease [13–16].

Hybrid pigments could also be obtained by the adsorption of basic (C.I. Reactive Blue 19) or acidic (C.I. Acid Violet 1, C.I. Acid Red 18 and C.I. Acid Green 16) dyes on the surface of the silica precipitated from a solution of sodium silicate and carbon dioxide in the presence of ethylene glycol. In the study reported in [17] prior to the dye adsorption the silica was modified. The pigments obtained were characterised as to the structure and particle size distribution. SEM study proved high uniformity of the pigment particles. The pigments were also highly stable.

Besides silica and titania, kaolin and aluminium oxide are also used as dye supports. Harris et al. [18] analysed the ability of these two supports to adsorb dyes. These authors supported 23 organic dyes from water solutions on the surface of kaolin or aluminium oxide. From among the 23 dyes studied as many as 22 were better adsorbed on the surface of kaolin than on aluminium oxide (for 8 the adsorption was up to 7 times greater and for 5 even up to 20 times greater). Four of the 23 dyes (3,6–diaminoacridine, 9–aminoacridine, azure–A or C.I. Basic Red 2) were used for the further study of the effect of pH on the efficiency of adsorption on gibbsite or silica at pH = 9. The dyes were selectively adsorbed on kaolin in the whole pH range studied and at pH above 9 their adsorption on kaolin was better than on aluminium oxide, gibbsite or silica. The structure of kaolin crystals studied applying the XRD method before and after adsorption of 3,6–diaminoacridine on its surface was found unchanged. This observation means that the dye particles are not intercalated in packet structures but are retained on the kaolin surface due to the opposite charges of the surface (negative) and the dye (positive).

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Hybrid pigments made of silica and organic dye are promising substrates for the obtaining of nonlinear optical materials, chemical sensors, coloured filters and luminescence sunlight collectors. Recently, studies have been undertaken to check which parameters ensure getting hybrids of the most desirable properties. Hirashima et al. [19] studied the structure and functionalities of silica gel obtained from alcohol solution of phenyltriethoxysilane (PhTES) and tetraethoxysilane (TEOS) and the dyes adsorption on its surface. The pyrene dyes and C.I. Basic Violet 10 were introduced directly into the solution from which the xerogel was precipitated. The xerogel structure was studied by IR and UV spectroscopies. The best results were obtained for the ratio $[PhTES]/[PhTES + TEOS] < 0.3$; the xerogel obtained was the most stable and the dye was practically not eluted in ethanol solution. The number of Si–Ph bonds increased with increasing concentration of PhTES in the initial solution.

Some pigments besides the property of colouring also show luminescence properties or can change colour with temperature. These pigments are used for the production of luminescent or thermometric paints. Inorganic oxide pigments are highly resistant to light, chemical substances and weather. With the help of pigments an unlimited practical number of colour combinations can be obtained. Pigments are also used for ionic coloration of glasses, UV stabilisation of coatings, plastics, foils and colour toners (with nanocrystalline zinc oxides) [20].

In this paper we present the results of studies performed to obtain hybrid pigments by adsorption of C.I. Mordant Red 3 on both unmodified and *N*-2-(aminoethyl)-3-aminopropyltrimethoxy silane–modified silica supports.

2. Experimental

2.1. Silica support preparation

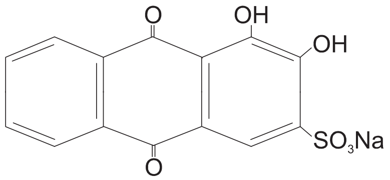
Two types of emulsions were prepared. The first one labelled as E2 and referred to as acidic was composed of the organic phase (cyclohexane POCh SA) and a 5% solution of hydrochloric acid (POCh SA). It also included nonylphenylpolyoxyethyleneglycol ethers (NP3 and NP6, PCC ROKITA SA). The second emulsion labelled E1 was referred to as the basic one. It contained a fixed volume of a 20% solution of sodium silicate (VITROSILICON SA) into which cyclohexane and emulsifiers (NP3 and NP6) were introduced in appropriate amounts. The emulsions were obtained by dissolving weighted portions of non-ionic surfactants in cyclohexane. The mixture obtained was applied in small doses into the water phase being a water solution of sodium silicate for E1 and a water solution of hydrochloric acid for E2. The E2 emulsion was homogenised in the next step for 20 min at the rate of 8800 rpm and placed in a reactor (QVF MiniPlant Pilot-Tec) of 10 dm^3 in capacity (under continuous stirring at the rate of 760 rpm). Then, E1 was homogenised at the rate of 8800 rpm for 20 min. After this stage, E1 was introduced in doses into E2 at the rate of 20 cm^3/min using a peristaltic pump. As a result of dispergation a white sediment of silica appeared, which was later destabilised at 80 °C in order to separate the organic phase. The sample was filtered off under reduced pressure. The filtration residue obtained was washed a few times with hot water and then with methanol in order to remove possible residues of surfactants. The last phase of the process was the removal of humidity from the silica by spray drying in a GeoNiro A/S.

2.2. Silica surface modification

The modification of silica surface was performed in a reactor containing 20 g of silica support and a solution of the modifying compound. The solution contained *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D) in the amount of 3 weight parts by mass and a certain amount of the solvent of water and methanol mixed at the 1:4 (v/v) ratio. The modification was performed in a mixer according to the earlier described procedure [21].

2.3. Hybrid pigments preparation

The hybrid pigments were obtained using the C.I. Mordant Red 3 (Alizarin Red S, ARS), purchased from Sigma–Aldrich, of the following formula:



To an adsorber containing 7.5 g of modified or unmodified silica support, a portion of 250 cm^3 of C.I. Mordant Red 3 of appropriate concentration in ethanol was added (the ethanol solutions of the following dye concentrations were prepared 20, 40, 60, 80, 100, 500, 1000, 1500, 2000 or 3000 mg/dm^3). The solvent was additionally acidified by a proper amount of hydrochloric acid. The suspension was stirred for 2 h by a magnetic stirrer IKAMAG R05 made by IKA Werke GmbH. The suspension was filtered off under reduced pressure and the washed sediment was dried in a stationary drier for 24 h, at 105 °C. In the filtrate the concentration of not adsorbed dye was determined by absorbency measurements using a SPEKOL 1200 spectrophotometer, made by Analytik Jena.

The next step was the evaluation of stability of the hybrid pigments (elution test).

To a conical flask of 200 cm^3 in capacity, containing 20 cm^3 of ethanol, a portion of 0.1 g of the pigment hybrid obtained was added. The suspension was mixed by a magnetic stirrer IKAMAG R05 made by IKA Werke GmbH for an hour at room temperature. The suspension was filtered under reduced pressure. In the filtrate the concentration of the soluble components was evaluated by absorbency measurements on SPEKOL 1200 spectrophotometer. The concentration of the eluted dye was read off from the calibration curve.

2.4. Physico-chemical properties

The precipitated silica support and the hybrid pigments obtained were characterised as to their physico-chemical properties. Their particle size distributions were determined by a Zetasizer Nano ZS apparatus made by Malvern Instruments Ltd., operating on the basis of the light non-invasive back scattering phenomenon (NIBS). On the basis of the particle size distribution the polydispersity index of

Table 1
The adsorption efficiency and degree of C.I. Mordant Red 3 elution from both unmodified and aminosilane-grafted silica supports (*W* – efficiency, *X* – degree of elution).

Initial dye concentration (mg/dm^3)	Unmodified silica		Modified silica	
	W (%)	*X* (%)	*W* (%)	*X* (%)
20	56.00	43.50	65.50	30.95
40	87.75	15.59	88.55	11.30
60	93.16	10.89	94.38	9.20
80	97.50	9.60	97.78	8.45
100	97.60	7.58	97.98	6.80
500	98.10	2.85	98.44	1.17
1000	99.06	1.58	99.17	0.92
1500	99.16	0.97	99.25	0.46
2000	99.19	0.87	99.37	0.35
3000	99.31	0.62	99.41	0.21

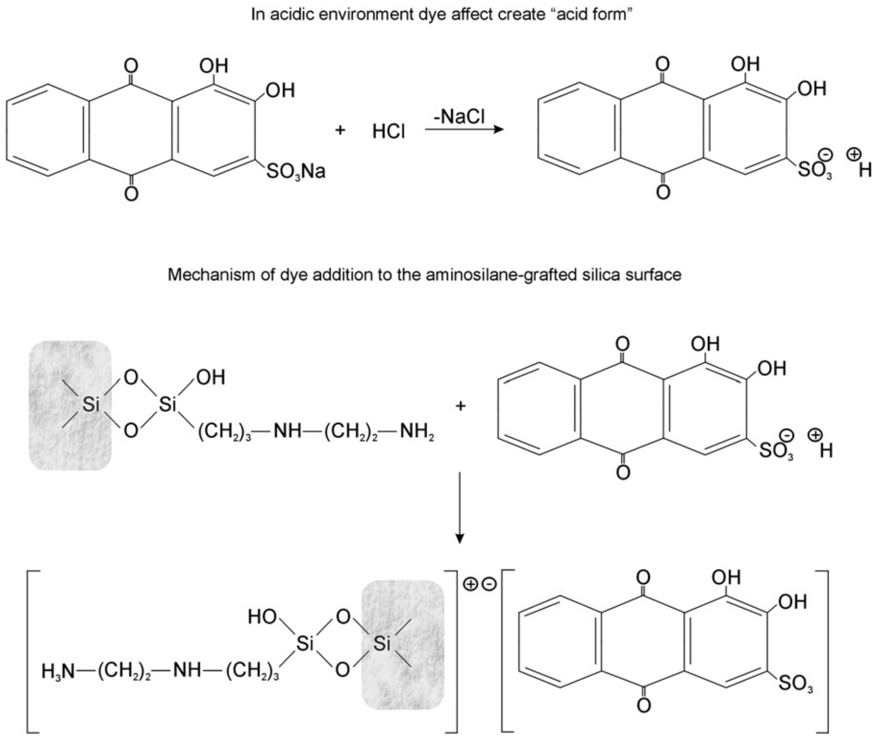


Fig. 1. The electrostatic interaction between the dissociated anion of dye and the cation appearing on the silica surface modified with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane.

the material studied was obtained. With the help of Zetasizer Nano ZS it was also possible to measure the electrophoretic mobility and indirectly the zeta potential (Zetasizer Nano ZS software gives the possibility to calculate electrophoretic mobility values into the zeta potential based on the Henry equation). The particle sizes were also measured by an analyser Mastersizer 2000, measuring particles of the sizes from 0.02 to 2000 micrometers. The morphology and microstructure of the silicas precipitated and randomly selected pigment samples were analysed using a scanning electron microscope Zeiss VO40. The observations permitted the evaluation of dispersion degree, structure of particles and their tendency towards aggregation or agglomeration.

Specific surface area A_{BET} (based on BET isotherm equation) was measured by a low-temperature adsorption of nitrogen. The isotherms of nitrogen adsorption/desorption were measured at 77 K using an ASAP 2020 apparatus made by Micromeritics Instruments Co.

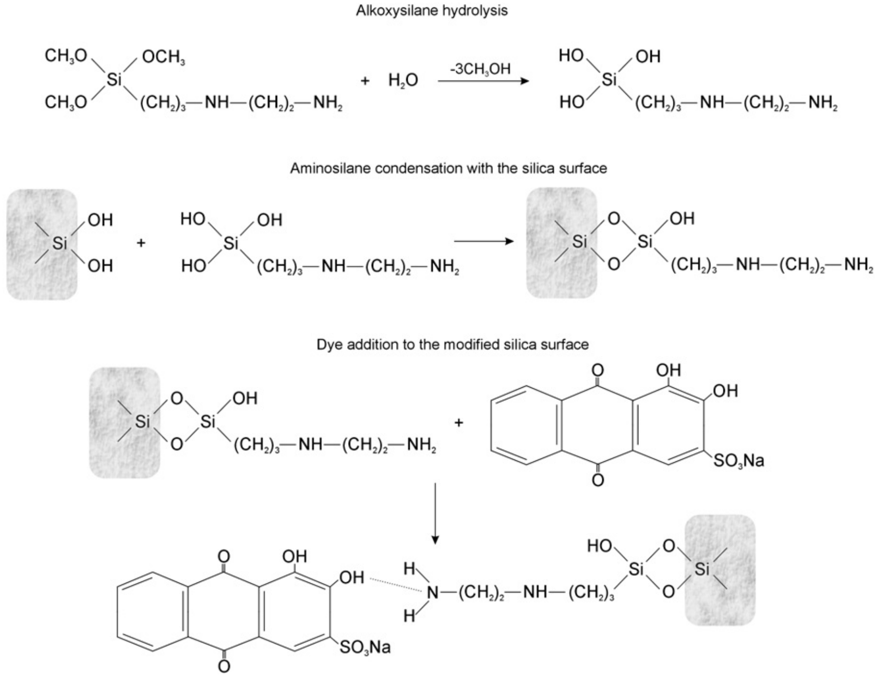


Fig. 2. The hydrogen bond formation mechanism between C.I. Mordant Red 3 and the modified silica support.

The degree of modification and the silica support covering with the dye were estimated using FT–IR EQUINOX 55 spectrophotometer made by Bruker. The silica supports and the hybrid pigments obtained were subjected to IR analysis, for the material suspended in carbon tetrachloride as this compound has little IR absorption in the range of IR absorption of the pigment sample. The suspension concentration, the time of the suspension stability in CCl_4 and the rate of its sedimentation are the important parameters used in this method. For the materials studied the best results were obtained for a 4% suspension concentration.

The wettability with water of the powdered material was estimated to check the hydrophilic or hydrophobic character of the surface. The measurements were performed for 1000 s by a K100 tensiometer (Krüss) with appropriate equipment. Chemical composition of the silica support samples and pigments was carried out by an Elementar model Vario EL III apparatus.

The colorimetric data of the obtained hybrid pigments were documented using an instrumented colorimeter (Specbos 4000, JETI Technische Instrumente GmbH), which was calibrated using a white colour standard tile with tristimulus values: $X = 80.56$, $Y = 84.85$, and $Z = 87.41$ (Standard no. 0085). Daylight (D65) was used as a standardised light source. A fixed amount of pigment sample was poured into the measurement cup. The instrument evaluated the colour in terms of the CIE $L^*a^*b^*$ colour space system. In this colour space, L^* represents the brightness, a^* and b^* are colour coordinates, where $+a^*$ is the red direction, $-a^*$ the green direction, $+b^*$ the yellow direction, and $-b^*$ is the blue direction. Moreover, changes in individual components allowed estimation of the total change in colour ΔE^*. The symbol C^* stands for chrome and h^* for the hue.

3. Results and discussion

At the first stage of these studies the efficiency of dye adsorption on both modified and unmodified silica was established.

Table 1 presents the adsorption efficiencies and degrees of C.I. Mordant Red 3 elution from the inorganic support. The dye adsorption was performed on both modified and unmodified silica in a wide range of dye concentrations, from 20 to 3000 mg/dm^3. The efficiency of dye adsorption increases with its increasing concentration in the initial solution. The yield was only 56.00% when the dye solution of 20 mg/dm^3 concentration was used,

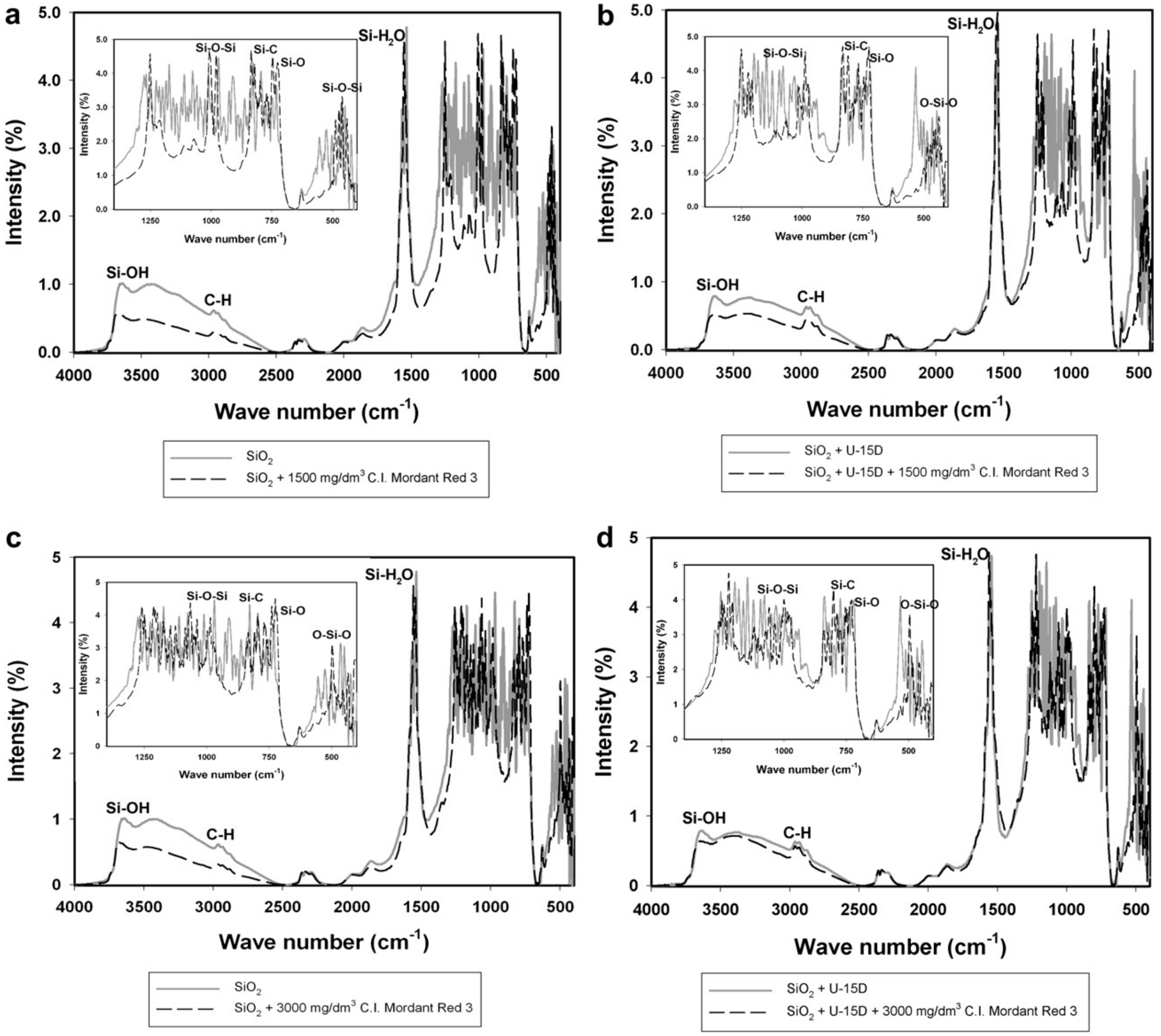


Fig. 3. The FT–IR spectrum of both unmodified and aminosilane-modified SiO_2 and supports with C.I. Mordant Red 3 adsorbed from the initial solution concentrations: (a, b) 1500 mg/dm^3 and (c, d) 3000 mg/dm^3.

whereas using a solution of 3000 mg/dm^3, the efficiency was 99.31%. Modification of the silica surface also resulted in an increase in the dye adsorption efficiency, e.g. for C.I. Mordant Red 3 concentration of 20 mg/dm^3 in the initial solution, the efficiency increased from 56% (unmodified SiO_2) to 65% (aminosilane-grafted silica). For the pigment obtained from the dye solution of the highest concentration (3000 mg/dm^3) the effect of silica surface modification was smaller. The degree of dye elution from the SiO_2 support is greater in the unmodified than in the modified silica, e.g. for C.I. Mordant Red 3 in the concentration of 20 mg/dm^3 in the initial solution, the degree of its elution from the unmodified support is 43.50%, while from the modified silica it is 30.95%. The degree of the dye elution decreases with increasing dye concentration in the initial solution. The adsorption of dye was particularly stable when it was supported on aminosilane-grafted SiO_2. After adsorption from the dye solutions of high concentrations its elution from the silica support was low (below 1%).

Chemical adsorption of the C.I. Mordant Red 3 on the surface of modified silica is most probably realised by the formation of an electrostatic bond between the dissociated anion of the dye and the cation of the amine group of silane being the modifying agent of silica (Fig. 1). The degree of the dye elution from the surface of unmodified silica is significantly greater than that from a modified one. This observation can suggest that the adsorption of dye on the unmodified silica surface has a physical character, i.e. that between the amine group on the modified SiO_2 and the hydroxyl group of dye a hydrogen bond develops. Schematic illustration of this mechanism is presented in Fig. 2.

The FT–IR spectrum (Fig. 3) proves the presence of vicinal silanol groups (high intensity band at 3660 cm^{-1}). Modification of the silica surface and adsorption of the dye from the solutions of concentrations of 1500 or 3000 mg/dm^3 results to a decrease in the intensity of the band assigned to silanol groups. The intensity of the band at 3660 cm^{-1} is more reduced with the adsorption of dye on modified silica (Fig. 3b and d). The spectrum also shows the bands assigned to the stretching vibrations ν(C–H) at 2965 e 2850 cm^{-1}. The band at 2965 e 850 cm^{-1} in the FT–IR spectrum of the dye attached to modified silica is more intense than that of the same dye adsorbed on unmodified silica. The reduced intensity of the band assigned to silanol groups (3660 cm^{-1}) after silica modification and dye adsorption indicates the chemical nature of the reaction on the support surface. An additional confirmation of this fact is the increase in intensity of the band characteristic of siloxane groups (≡Si–O–Si≡).

Elemental analysis (Table 2) evidenced the presence of such elements as C, H and S on the surface of pigments (at the dye concentration of 1000 mg/dm^3) obtained on unmodified silica support. The presence of sulphur followed by the structure of C.I. Mordant Red 3 ($C_{14}H_8O_4SO_3Na$). On the surface of pigments obtained using modified silica (modification with 3 weight parts by mass of N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, see Table 3) the presence of C, H, S and N was found. The carbon content enabled, calculating the extent of silica surface coverage using the equation by Berendsen and de Golan [22]. The presence of nitrogen obtained from the use of aminosilane for SiO_2 surface modification. According to the plot shown in Fig. 4, the degree of silica coverage with the adsorbed dye increases with increasing concentration of C.I. Mordant Red 3 in the initial solution. The modification of the silica surface has a positive effect on the adsorption and on the degree of coverage. For the hybrid pigments obtained as a result of adsorption of dye at the lowest concentration on inorganic support (20 mg/dm^3), the degree of coverage increased from 1.36 (unmodified silica) to 2.54 μmol/m^2 (modified silica), while for the pigment obtained as a result of adsorption of the dye in the highest concentration (3000 mg/dm^3) the degree of coverage increased from 3.42 to 5.49 μmol/m^2.

Table 2
Elemental content and the coverage degree of the unmodified silica surface with the C.I. Mordant Red 3.

Initial dye concentration (mg/dm^3)	Content (%)			Degree of coverage (μmol/m^2)
	C	H	S	
20	1.595	1.352	–	1.36
40	1.601	1.354	–	1.37
60	1.606	1.357	–	1.37
80	1.638	1.368	–	1.40
100	1.656	1.377	–	1.42
500	1.942	1.382	–	1.67
1000	2.274	1.387	0.118	1.97
1500	2.987	1.401	0.327	2.63
2000	3.519	1.415	0.435	3.13
3000	3.822	1.513	0.522	3.42

Table 3
Elemental content and the coverage degree of the modified silica surface with the C.I. Mordant Red 3.

Initial dye concentration of (mg/dm^3)	Content (%)				Degree of coverage (μmol/m^2)
	N	C	H	S	
20	–	2.892	1.517	–	2.54
40	–	2.923	1.528	–	2.57
60	–	2.940	1.542	–	2.58
80	0.278	2.967	1.557	–	2.61
100	0.283	2.983	1.560	–	2.62
500	0.291	3.657	1.572	–	3.26
1000	0.295	4.326	1.598	0.176	3.92
1500	0.301	4.923	1.621	0.386	4.52
2000	0.309	5.322	1.655	0.437	4.93
3000	0.315	5.848	1.704	0.594	5.49

Harris et al. have studied adsorption of C.I. Mordant Red 3 on kaolin and QAL alumina. The pigments they obtained were characterised with the degree of coverage of 1.70 μmol/m^2 for kaolin and 1.25 μmol/m^2 for QAL alumina [18]. With the functionalised support obtained according to the procedure proposed in this work the degree of coverage with the dye could be up to three times higher.

The colorimetric analysis in the CIE $L^*a^*b^*$ colour space system provided the information on the colorimetric data of the pigments obtained (Table 4). The pigments were dark red, so an increase in the contribution of red colour ($+a^*$) was observed with increasing concentration of dye in the initial solution. The contribution of blue

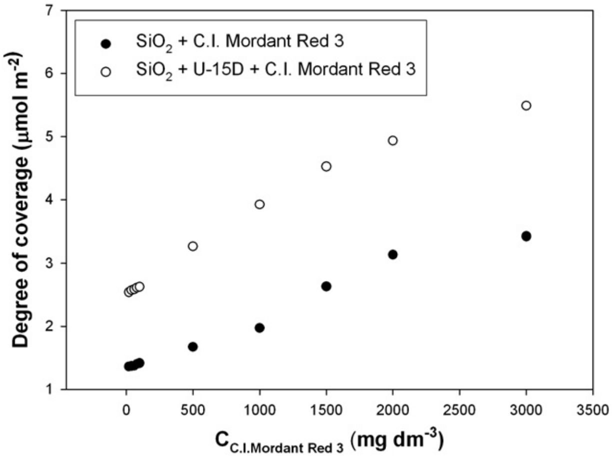


Fig. 4. The coverage degree of both modified and unmodified silica surface with the C.I. Mordant Red 3 versus the initial concentration of the dye solution used (specific surface area of the silica support was 72 m^2/g).

Table 4
Colorimetric data of the unmodified (modified) silica and hybrid pigments obtained using C.I. Mordant Red 3 solutions of different concentrations.

Initial dye concentration (mg/dm^3)	Colorimetric data											
	L^*		a^*		b^*		C^*		h^*		ΔE^*	
	SiO_2	SiO_2 + U-15D	SiO_2	SiO_2 + U-15D	SiO_2	SiO_2 + U-15D	SiO_2	SiO_2 + U-15D	SiO_2	SiO_2 + U-15D	SiO_2	SiO_2 + U-15D
0	94.01	93.91	−0.12	−0.02	2.86	2.19	3.01	2.19	92.34	86.85	–	–
20	82.34	91.29	7.00	5.38	0.23	−0.07	7.00	5.38	351.91	359.20	13.94	6.71
40	82.29	85.27	8.33	7.38	−0.41	−1.74	8.34	7.58	357.17	346.71	14.85	12.29
60	79.65	84.77	8.91	8.14	−1.07	−1.79	8.98	8.34	353.13	347.63	17.44	13.13
80	78.32	84.22	9.29	8.63	−1.53	−1.80	9.41	8.82	350.62	348.22	18.85	13.82
100	78.29	83.86	9.86	10.06	−1.34	−2.22	9.95	10.30	352.25	347.57	19.12	15.13
500	67.54	72.54	15.61	15.96	−2.69	−3.72	15.48	16.39	350.24	346.88	31.31	27.50
1000	61.51	69.35	17.75	19.58	−3.50	−3.69	18.09	19.93	348.86	349.32	37.65	32.11
1500	57.99	61.65	19.08	21.12	−3.30	−4.08	19.36	21.51	350.19	349.07	41.30	39.21
2000	55.25	60.45	20.28	21.93	−2.99	−3.93	20.50	22.28	351.62	349.85	44.21	40.60
3000	48.47	52.28	20.47	21.86	−3.41	−4.69	20.76	22.36	350.54	347.88	50.38	47.64

($-b^*$) also grew. The brightness of the pigments decreased with increasing concentration of C.I. Mordant Red 3 in the initial solution; e.g. for the pigment obtained by adsorption of dye from the solution of its lowest concentration 20 mg/dm^3 on unmodified silica, the value of L^* was 82.34, whereas for the pigment obtained with the use of dye solution concentration of 3000 mg/dm^3 it was 48.47. The contribution of red colour for the pigment obtained on the unmodified silica with the use of dye solution of 20 mg/dm^3 was 7.0, whereas that for the pigment obtained on the modified silica, was 5.38. For the pigment obtained by adsorption of C.I. Mordant Red 3 from a solution of 3000 mg/dm^3 on the unmodified silica the contribution of red colour was 20.47, whereas for the pigment obtained on the modified SiO_2 it increased to 21.86. The increase in the contribution of blue colour is lower than that in red. The contributions of these two colours increased more for pigments obtained using modified silica.

Analogous relations were observed for the parameter C^*. Saturation of the colour of the pigments obtained increased in proportion to the concentration of the dye in the initial solution (from 7.00 – SiO_2 + 20 mg/dm^3 of C.I. Mordant Red 3 to 20.76 – SiO_2 + 3000 mg/dm^3 of C.I. Mordant Red 3). Slightly higher values of this parameter (especially at higher concentrations of the dye solution to be adsorbed) were obtained for the dye attached to modified silica support. The hue of the pigments depends mainly on their morphology and degree of dispersion, therefore, the hue estimates do not correlate with the other colorimetric parameters and the

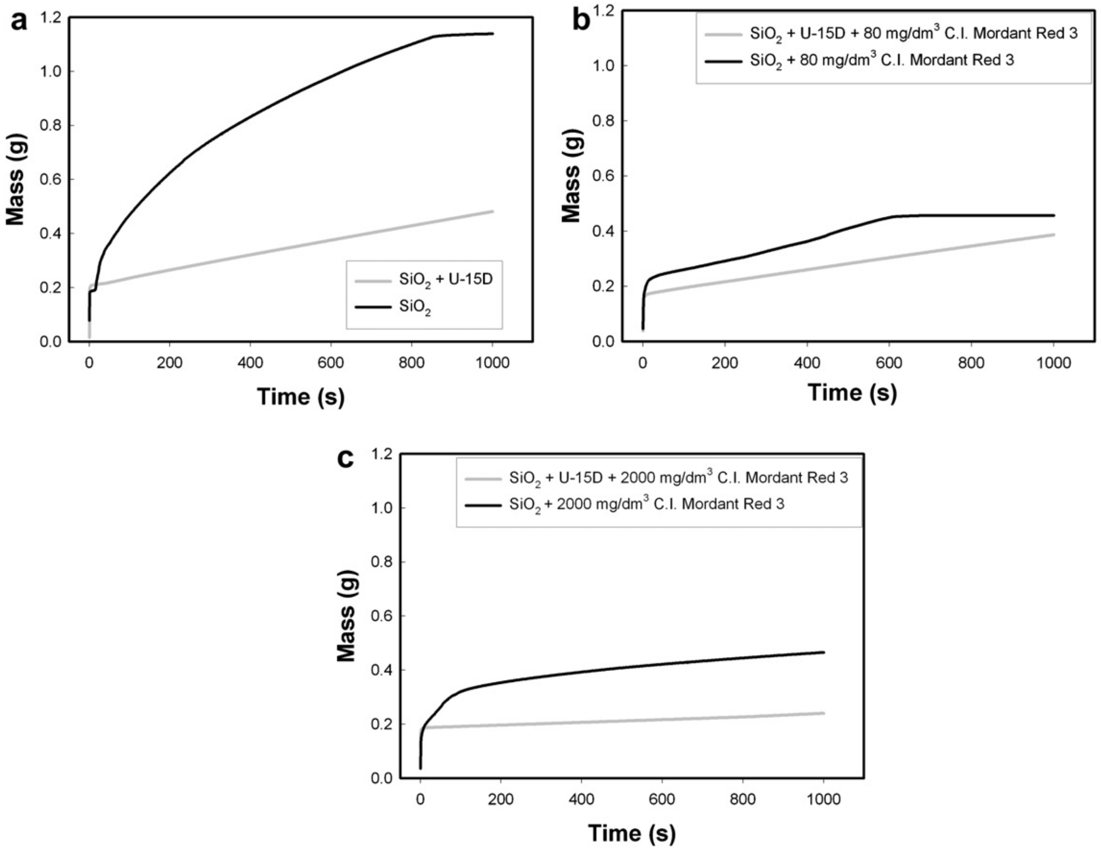
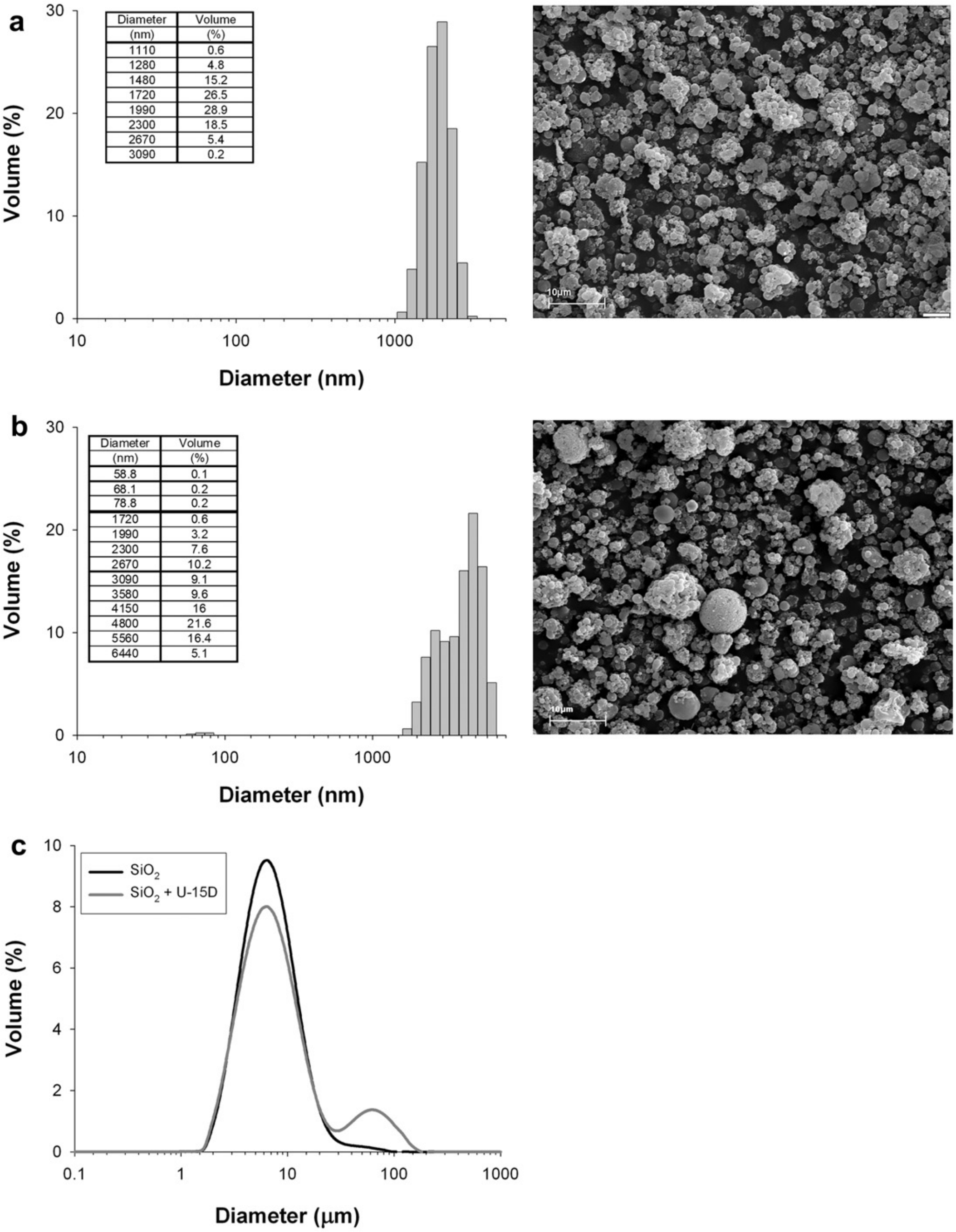


Fig. 5. Wettability with water of (a) unmodified and aminosilane-functionalised SiO_2; hybrid pigments obtained by C.I. Mordant Red 3 adsorption from the solutions of (b) 80 mg/dm^3 and (c) 2000 mg/dm^3 both on unmodified and modified silica supports.

initial concentration of dye in the solution. Total change in the colour of the pigments, estimated with ΔE^* parameter, also depends on the concentration of the dye adsorbed. Higher values of ΔE^* were noted for the dyes supported on unmodified silica, which can be explained by the fact, that the adsorption of aminosilane reduces the L^* parameter and contributes to its total change in colour.

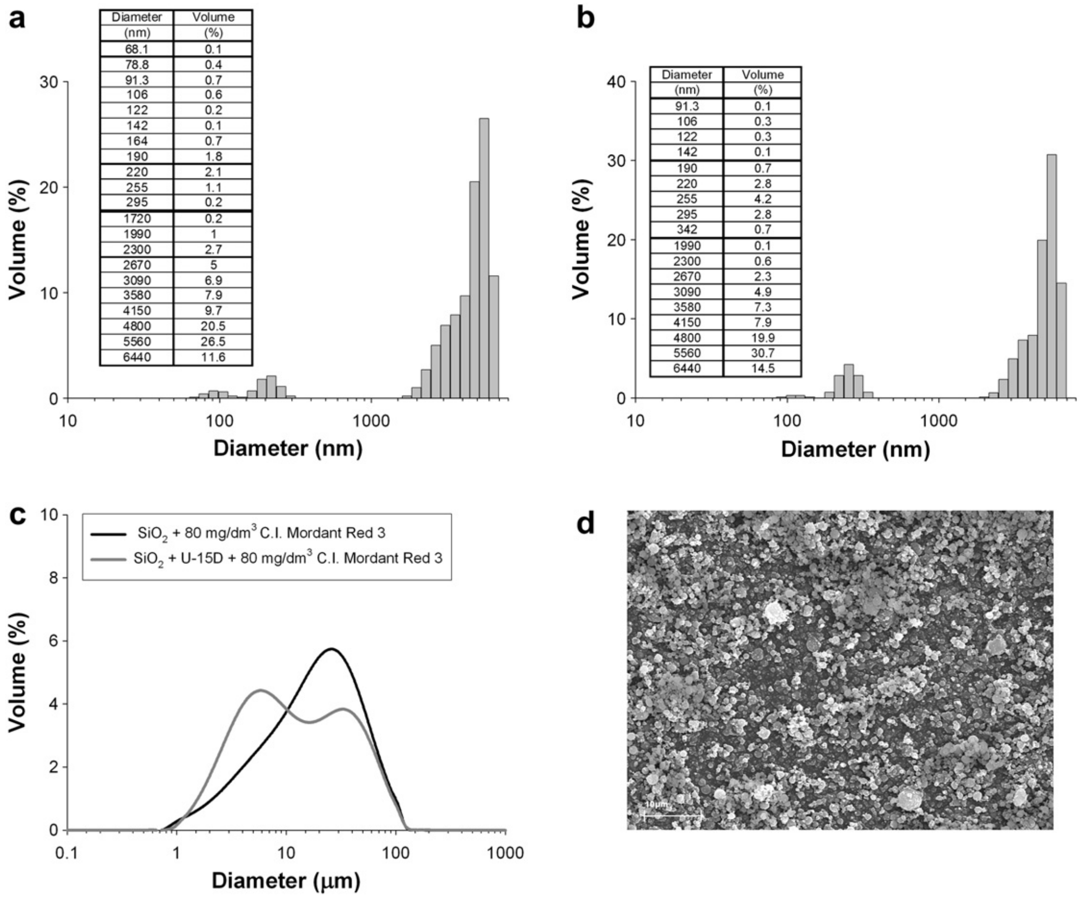
The wettability with water of the initial silicas and the pigments was tested to evaluate the hydrophobic or hydrophilic character of the surface of the products obtained. According to the data shown in Fig. 5a the mass increase in time is smaller for the modified silica, so it has lower affinity to water than the unmodified one. Thus, modification has resulted in hydrophobisation of the silica surface. The mass increase was also lower for the pigments than for the silica adsorbents. Fig. 5b and c presents the mass increase in time for the pigments obtained by the adsorption of C.I. Mordant Red 3 in the initial solution concentration of 80 and 2000 mg/dm^3 on both modified and unmodified silicas. The mass increase is smaller for the pigments obtained using the modified silica, which is the most pronounced for the pigment obtained by dye adsorption from a water solution of the concentration 2000 mg/dm^3. It means that the pigments obtained after adsorption of C.I. Mordant Red 3 on the modified silica are more hydrophobic.



Diameter (nm)	Volume (%)
1110	0.6
1280	4.8
1480	15.2
1720	26.5
1990	28.9
2300	18.5
2670	5.4
3090	0.2

Diameter (nm)	Volume (%)
58.8	0.1
68.1	0.2
78.8	0.2
1720	0.6
1990	3.2
2300	7.6
2670	10.2
3090	9.1
3580	9.6
4150	16
4800	21.6
5560	16.4
6440	5.1

Fig. 6. Particle size distributions and SEM microphotographs of (a) unmodified silica, (b) modified silica and (c) comparison of micrometric particle size distributions of both supports.



a

Diameter (nm)	Volume (%)
68.1	0.1
78.8	0.4
91.3	0.7
106	0.6
122	0.2
142	0.1
164	0.7
190	1.8
220	2.1
255	1.1
295	0.2
1720	0.2
1990	1
2300	2.7
2670	5
3090	6.9
3580	7.9
4150	9.7
4800	20.5
5560	26.5
6440	11.6

b

Diameter (nm)	Volume (%)
91.3	0.1
106	0.3
122	0.3
142	0.1
190	0.7
220	2.8
255	4.2
295	2.8
342	0.7
1990	0.1
2300	0.6
2670	2.3
3090	4.9
3580	7.3
4150	7.9
4800	19.9
5560	30.7
6440	14.5

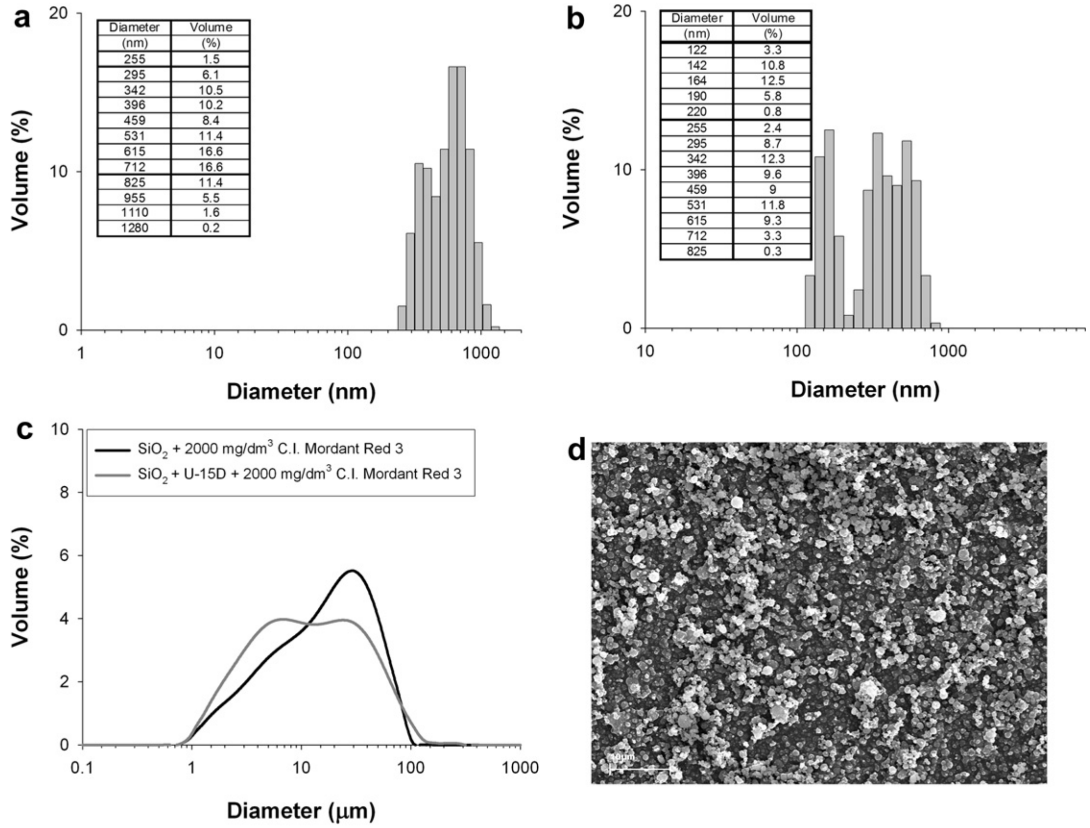
Fig. 7. Particle size distributions according to volume contribution of the pigments obtained after the C.I. Mordant Red 3 adsorbed from the solution concentration of 80 mg/dm^3 on (a) unmodified and (b) modified silica supports, (c) comparison of the micrometric particles size distributions according to volume contribution of the two hybrid pigments, (d) SEM microphotograph of the pigment obtained using modified silica.

The particle size distribution according to the volume contribution (Fig. 6a) of the unmodified silica shows a single band covering the diameter range 1110 e 3090 nm. The surface modification resulted in an increase in the volume contribution of secondary agglomerates, so a band appeared covering the diameters 1720 e 6440 nm (Fig. 6b). The particle size distribution of the modified silica also shows a band corresponding to the primary particles of the diameters 58.8 e 78.8 nm. These data were confirmed by the measurements made using Mastersizer 2000. Fig. 6c confirms to an increase in the volume contribution of secondary agglomerates as a result of the silica surface modification. Fig. 6a and b also show SEM microphotographs of the unmodified and modified silicas. The particles have spherical shape and show a tendency towards agglomeration. The polydispersity of the modified silica was 0.156 and for the unmodified one – 0.061.

The particle size distribution of the pigment obtained by adsorption of C.I. Mordant Red 3 from a solution of the initial concentration of 80 mg/dm^3 on the unmodified silica (Fig. 7a) shows two bands. The first should be assigned to primary particles and primary agglomerates (68.1 e 295 nm), whereas the second one to the secondary agglomerates (1720 e 6440 nm). The particle size distribution of the pigment obtained using the modified silica (Fig. 7b) shows three bands corresponding to the particles and agglomerates of diameters 91.3 e 142 nm, 190 e 342 nm and 1990 e 6440 nm. The volume contribution of secondary agglomerates is however lower then for the pigments obtained using the unmodified silica, Fig. 7a. The particle size distribution for the pigment on the modified silica indicates an increase in the volume contribution of particles of smaller diameters, whereas the contribution of secondary agglomerates decreases, Fig. 7c. The SEM microphotograph of the pigment obtained by the adsorption of C.I. Mordant Red 3 from the solution of the concentration of 80 mg/dm^{3}on the unmodified silica is given in Fig. 7d. The particles have spherical shape and show high tendency towards agglomeration (polydispersity index of 0.891).

The pigment obtained by the adsorption of C.I. Mordant Red 3 from the solution of the concentration of 2000 mg/dm^{3}on the modified silica had particles of smaller diameters. The particle size distribution of this pigment, presented in Fig. 8b, shows a single band covering the diameters range 122 e 825 nm, assigned to primary particles and agglomerate structures. The pigment obtained using the unmodified silica (Fig. 8a) has particles of larger diameters (255 e 128 nm). Fig. 8c confirms a decrease in the volume contribution of particles of large diameters as a result of the silica modification. The SEM microphotograph displayed in Fig. 8d proves that the pigment obtained on the modified silica has more uniform particles of spherical shape and small diameters. The sample polydispersity index is 0.470.

Fig. 9 presents changes in the zeta potential as a function of pH of the unmodified silica, of that modified with 3 weight parts by mass of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane and of the pigments obtained on the above silica supports by the adsorption of C.I. Mordant Red 3 from solutions of the concentration of 20 mg/dm^3 and 2000 mg/dm^3 (Fig. 9a). The adsorption of the dye from either of these solutions on the unmodified silica has no significant effect on the course of electrokinetic curves.



Diameter (nm)	Volume (%)
255	1.5
295	6.1
342	10.5
396	10.2
459	8.4
531	11.4
615	16.6
712	16.6
825	11.4
955	5.5
1110	1.6
1280	0.2

Diameter (nm)	Volume (%)
122	3.3
142	10.8
164	12.5
190	5.8
220	0.8
255	2.4
295	8.7
342	12.3
396	9.6
459	9
531	11.8
615	9.3
712	3.3
825	0.3

Fig. 8. Particle size distributions according to volume contribution of the pigments obtained after the dye adsorption from the solution concentration of 2000 mg/dm^{3}on (a) unmodified and (b) modified silica supports, (c) comparison of the micrometric particles size distributions according to volume contributions of the two pigment types and (d) SEM microphotograph of the pigment obtained using modified silica.

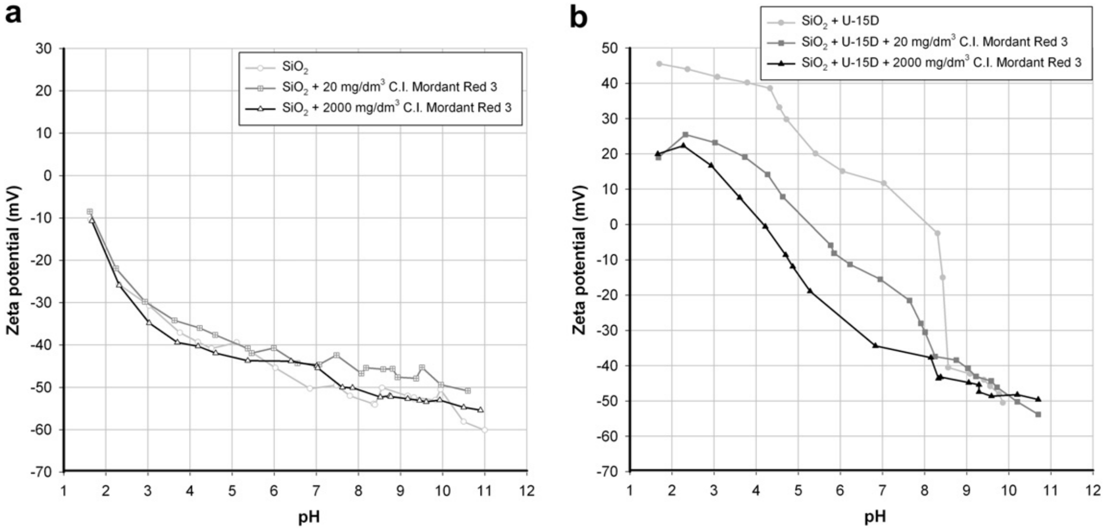


Fig. 9. Zeta potential vs. pH of (a) unmodified silica and pigments obtained on this support and (b) modified silica and hybrid pigments obtained on aminosilane-functionalised silica.

A significant shift of the isoelectric point towards neutral pH was observed after the adsorption of dye in the initial concentration of 20 and 2000 mg/dm^3 on the surface of the modified silica (Fig. 9b). The isoelectric point for the pigment obtained after adsorption of the dye from the solution of the concentration 20 mg/dm^3 is 5.4, whereas for that, prepared after the adsorption of dye from the solution of 2000 mg/dm^3 it is 4.2. The unmodified silica as well as the pigments obtained on this support have a negative zeta potential in the studied pH range.

4. Conclusions

The modification of the silica surface with *N*-2-(aminoethyl)-3-aminopropyl-trimethoxysilane caused an increase in the tendency towards the agglomeration of particles as the band assigned to the secondary agglomerates of the diameter range 1110 e 3090 nm shifted to 1720 e 6440 nm.

The efficiency of adsorption and the degree of silica coverage with dye increased with increasing concentration of the dye in the initial solution. This effect is more pronounced when using the modified silica as a support in pigment preparation. The degree of the dye elution from the silica surface decreases with increasing concentration of the dye in the initial solution. Modification of the silica surface causes a decrease in the degree of the dye elution from the SiO_2 support, which is proved by the lower intensity of the band assigned to the silanol groups on the modified silica and pigments in the FT–IR spectrum.

The pigments obtained on the modified silica have more intense red colour than those of the unmodified ones. The pigments obtained after the adsorption of C.I. Mordant Red 3 from the solutions of concentrations of 80 and 2000 mg/dm^3 on the modified silica were characterised by small particles. The unmodified silica and pigments obtained on this support have negative zeta potential in the studied pH range. The pigment obtained on the unmodified silica by adsorption of the C.I. Mordant Red 3 from the solution of the concentration of 20 mg/dm^3 has the isoelectric point of 5.4, while the analogous one obtained after adsorption of the dye from the solution of the concentration 2000 mg/dm^3 has the isoelectric point of 4.2.

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