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Characterisation of pigments obtained by adsorption of C.I. Basic Blue 9 and C.I. Acid Orange 52 dyes onto silica particles precipitated via the emulsion route

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Abstract

The adsorption of C.I. Basic Blue 9 and C.I. Acid Orange 52 dyes onto the colloidal silica surface precipitated via emulsion route was investigated in an aqueous medium. Equation of Berendsen and de Golan permitted to establish adsorption isotherms on the basis of chemical composition of the studied substances. Using direct measurements of zeta potential as a function of pH, electrokinetic characteristics were estimated for the studied silica carriers and the obtained pigments. The performed studies on dispersion demonstrated that the produced organic–inorganic hybrid systems manifested a highly homogenous character and a relatively low tendency to form agglomerate structures. In addition, the studied pigments were subjected to a comprehensive colorimetric appraisal using the CIE $L^*a^*b^*$ colour space system.

Keywords: Colloidal silica; Modification; Cationic dyes; Adsorption; Organic–inorganic hybrids

1. Introduction

In recent years formation of organic–inorganic hybrid materials have presented significant problems. Substances of the type used to be produced first of all by adsorption of organic particles on an oxide (synthetic or mineral) substrate. Adsorption of organic compounds (e.g., organic dyes) reflects two principal variables: (i) type of interaction (covalent bond or physical forces), (ii) character of an inorganic carrier (SiO_2, SiO_2/TiO_2, Al_2O_3, clays and carbonated substances), its surface and dispersion properties.

A silica synthesised by the sol–gel technique plays the role of a selective adsorbent of organic dyes [1–4]. The carrier formed in this way is highly uniform and, first of all, contains spherical particles of low dimensions (100–500 nm). Applying a high pressure technique Costa et al. [5] modified the reaction and obtained composites with a silica matrix of very high density and hardness. In this case, the adsorbates involved Naphthazarin, Quazarin, and Rhodamine 6G. In order to amplify interactions between a dye (Rhodoamine B) and the carrier, Seçkin et al. [6] applied silica functionalised with γ-glycidoxypropyltrimethoxysilane. The grafting of Rhodamine B onto epoxy-functionalised matrix offered a suitable medium for hybrid pigment preparation. Moreover, the characteristics of the dye on the grafted silica remained unchanged after UV irradiation.

Carriers of enhanced photocatalytic properties were also obtained by the sol–gel reaction in the presence of tetraalkoxytitanate [7,8].

Application of the Ludox colloidal silica for preparations of pigments yielded particularly favourable results [9,10]. Substances obtained in this way manifested very

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highly uniform particles and, first of all, the particles were of a nanometric size.

On the other hand, silicas formed by precipitation from aqueous solutions of alkali metal silicates (mainly sodium water glass) provide an alternative to SiO_2 carriers obtained by the sol–gel technique. For example, Krysztafkiewicz et al. [11] conducted adsorption of C.I. Acid Red 18 and C.I. Acid Violet 1 dyes on the surface of amorphous silica SYLOID®244. In order to amplify the organic dye/carrier interactions modifiers were used, belonging to the group of alkoxysilanes with amino groups. Due to the modification of SiO_2 surface, maximum adsorption of the studied dyes amounted to 98.9 and 99.4%, respectively. Parida and Mishra [12] decided to modify silica with the polyethylene glycol, PEG-4000. On the so grafted silica they adsorbed styryl pyridinium dyes. In other studies [13], the interesting synthesis of silica was proposed directly in the medium of ethylene glycol with parallel modification of the precipitated silicon dioxide surface using 3-aminopropyltriethoxysilane or *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane. The applied C.I. Direct Red 81 dye was adsorbed with the maximum efficiency of 99.93%. Moreover, the pigment obtained in this way manifested high chemical resistance.

Mineral substances represent a broad range of selective adsorbents or carriers [14–19]. The substances manifest a highly advantageous surface charge, which can be modified at will and be operative in the adsorption, mainly of positively charged dyes. Unfortunately, in most cases the minerals demonstrate a high diameter of particles with a pronounced tendency for formation of larger accumulations, the so called aggregates or agglomerates.

In present investigations studies were performed on adsorption of the model organic dyes (C.I. Basic Blue 9 and C.I. Acid Orange 52) on an unmodified and a modified silica carrier, obtained by precipitation in an emulsion medium. Such silica exhibited augmented adsorption potential, maintaining the highly uniform particle size. First of all, the extent of dye adsorption and effects of the dyes on homogeneity of the obtained hybrid materials were evaluated.

2. Experimental details

2.1. Preparation and modification of silica carries

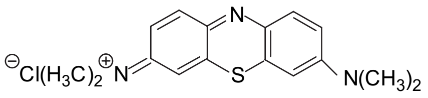
The reaction of silica synthesis was conducted using the two earlier prepared emulsions. Emulsion *I* contained aqueous solution of sodium metasilicate (VITROSILICON S.A.) and cyclohexane (POCh S.A.) while emulsion *II* consisted of hydrochloric acid (POCh S.A.) and cyclohexane. In each of the emulsions, the employed emulsifier involved a non-ionic surfactant from the group of oxyethylenated unsaturated fatty alcohols of the general formula: $RO(CH_2CH_2O)H$, $R = C_{16-22}$, $n \cong 7$ produced by the Chemical Works ROKITA S.A. The emulsions were prepared using a homogeniser, at 19,000 rpm.

The silica precipitation process was conducted in a reactor of 5 dm^3capacity, in which emulsion *II* was placed. Emulsion *I* was dosed at a constant rate and the reactive system was mixed using a ULTRA TURRAX T50 Basic homogeniser (IKA Labortechnik) at 10,000 rpm. The reaction was performed at room temperature and the silica was obtained in form of a third emulsion. The product was subjected to destabilisation at 80 °C, and the heated up mixture was distilled to remove the organic phase while the precipitated silica was subjected to filtration. The filtration cake was subjected to stationary drying at 105 °C for 48 h.

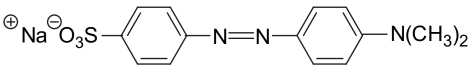
Surface modification of the silica precipitated in the emulsion system was implemented using *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15), produced by UniSil. In order to avoid aging, the silane was subjected to hydrolysis in a solution prepared directly before modification (methanol/water 4:1). The modification was performed in a specially constructed reactor [20] in the course of 1 h and the solvent was distilled off.

2.2. Hybrid pigment preparation

For the preparation of the organic–inorganic hybrids, C.I. Basic Blue 9 – Methylene Blue (POCh S.A.) and C.I. Acid Orange 52 – Methyl Orange (POCh S.A.) dyes were applied, of the following structure:



C.I. Basic Blue 9



C.I. Acid Orange 52

Adsorption of the dyes was performed on both unmodified and aminosilane-modified silica. The adsorption process was implemented changing concentration of the aqueous dye solutions in the range of 20–4000 mg/dm^3. The reaction SiO_2/organic dye was performed in 1 h, at room temperature, with parallel mixing using the magnetic stirrer. In the case of C.I. Acid Orange 52 adsorption on the modified silica the reaction was conducted in an acidic environment.

2.3. Physicochemical properties evaluation

The unmodified silica, aminosilane-grafted silica, and the obtained silica–dye hybrids were subjected to a broad physicochemical and morphological evaluation.

Specific surface areas of the unmodified silica and modified silica's powders were determined by N_2 adsorption (BET method) using ASAP 2010 instrument (Micrometrics Instrument Co.).

The silica materials and the organic–inorganic hybrids were characterised by the quantitative elemental analysis (C, N and S analysis) using a Vario EL III instrument (Elementar).

Zeta potentials were estimated by a direct measurement of electrophoretic mobility, employing the technique of electrophoretic light scattering (ELS) in the ZetaPlus apparatus (Brookhaven Instruments Co.). The experiment was performed at a constant ionic strength (0.001 M NaCl). A series of measurements was performed which permitted to establish zeta potential values for the studied colloidal substances. Each of the values represented a mean of ten direct measurements. The average error of the mean ranged between ± 1.0 and ± 1.5.

The multimodal particle (aggregate and agglomerate) size distribution was evaluated also in the ZetaPlus apparatus, employing the technique of a dynamic light scattering (DLS). On the other hand, polydispersity was calculated as a function of particle size distribution.

The colorimetric data of the obtained silica 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 provided the colour in the terms of the CIE $L^* a^* b^*$ colour space system. In this colour space, L^* represented the lightness (or brightness), a^* and b^* were colour coordinates, where $+a^*$ was the red direction, $-a^*$ was the green direction, $+b^*$ was the yellow direction, and $-b^*$ was the blue direction. Moreover, changes in individual components allowed to estimate the total change of colour ΔE^*. On the other hand, C^* denoted chrome, and h^* determined hue.

3. Results and discussion

3.1. Surface coverage

The performed elemental analysis permitted to determine amounts of carbon, nitrogen and sulphur in the studied silicas and in the obtained silica–organic dye hybrids. Moreover, it allowed calculating the extent of covering silica surface with respect to carbon using the equation of Berendsen [21].

The calculated specific surface area amounted to 182 and 119 m^2/g for the unmodified and the modified silica, respectively.

Results of elemental analysis of the unmodified silica and of pigments obtained on the carrier using Methylene Blue are presented in Table 1. Relatively high amounts of carbon were observed to be incorporated into the structure of unmodified silicon dioxide. This reflected the technology of precipitation of colloidal silica in an emulsion system, in which high amounts of carbon were introduced to the reaction system with the emulsifier (oxyethylenated fatty alcohol). In parallel, increase in concentration of the adsorbed dye (C.I. Reactive Blue 9) induced evident increases in the content of carbon and nitrogen. An increase was also observed in the content of adsorbate-originating sulphur but detection of the element was possible only when concentration of the dye reached 500 mg/dm^3.

Application of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane-modified silica as an adsorbent of Methylene Blue resulted in augmented selectivity of the adsorption. This was proven by detection of sulphur already at adsorption of C.I. Basic Blue 9 at the concentration of 60 mg/dm^3. In turn, adsorption of methyl orange (C.I. Acid Orange 52) on the surface of

Table 1
Dispersive and chemical properties of the unmodified SiO_2/C.I. Basic Blue 9 hybrid

Sample	Hybrid content	Dispersion evaluation			Elemental analysis		
		Mean particle diameter (nm)	Polydispersity	Effective particle diameter (nm)	Content (%)		
					C	N	S
1	SiO_2	565	0.095	431	9.183	–	–
2	$SiO_2 + 20\ mg/dm^3$ MB	536	0.044	416	9.203	0.017	–
3	$SiO_2 + 40\ mg/dm^3$ MB	714	0.142	432	9.246	0.019	–
4	$SiO_2 + 60\ mg/dm^3$ MB	556	0.107	412	9.356	0.023	–
5	$SiO_2 + 80\ mg/dm^3$ MB	548	0.126	392	9.398	0.024	–
6	$SiO_2 + 100\ mg/dm^3$ MB	468	0.034	391	9.452	0.026	–
7	$SiO_2 + 500\ mg/dm^3$ MB	308	0.005	334	9.982	0.201	0.097
8	$SiO_2 + 1000\ mg/dm^3$ MB	291	0.005	356	10.76	0.412	0.239
9	$SiO_2 + 1500\ mg/dm^3$ MB	277	0.081	300	11.06	0.574	0.428
10	$SiO_2 + 2000\ mg/dm^3$ MB	415	0.210	377	11.54	0.687	0.531
11	$SiO_2 + 4000\ mg/dm^3$ MB	262	1.276	415	12.23	0.785	0.612

silica pre-modified with U-15 silane progressed with satisfactory efficiency and in this case the detection was possible at any concentration of the applied dye.

Analysis of the extent of coverage, calculated as related to carbon using the equation of Berendsen (Fig. 1a and b), allowed to note an evident increase in adsorption of Methylene Blue on the aminosilane-coated SiO_2 surface when concentration of a dye exceeded 60 mg/dm^3. In this case, the extent of coating amounted to 0.101 μmol/m^2 and was fourfold higher than the extent of coating of the same silica with Methyl Orange (0.025 μmol/m^2). On the other hand, the extent of coating unmodified silica with Methylene Blue was 0.049 μmol/m^2. The results indicated that, as compared to the unmodified silica, the modified silica manifested a twofold higher extent of adsorption of the C.I. Basic Blue 9 dye. A more evident efficiency of adsorption was noted for dye concentrations of 80 or 100 mg/dm^3. After applying both of the analysed dyes at 4000 mg/dm^3 an augmented extent of coverage with Methylene Blue was noted. The extent of coverage with Methyl Orange was 0.261 μmol/m^2. Upon comparison of the value with the extent of coverage obtained for the twofold lower concentration of the dye (sample 31), the latter was found to be lower by 0.019 μmol/m^2.

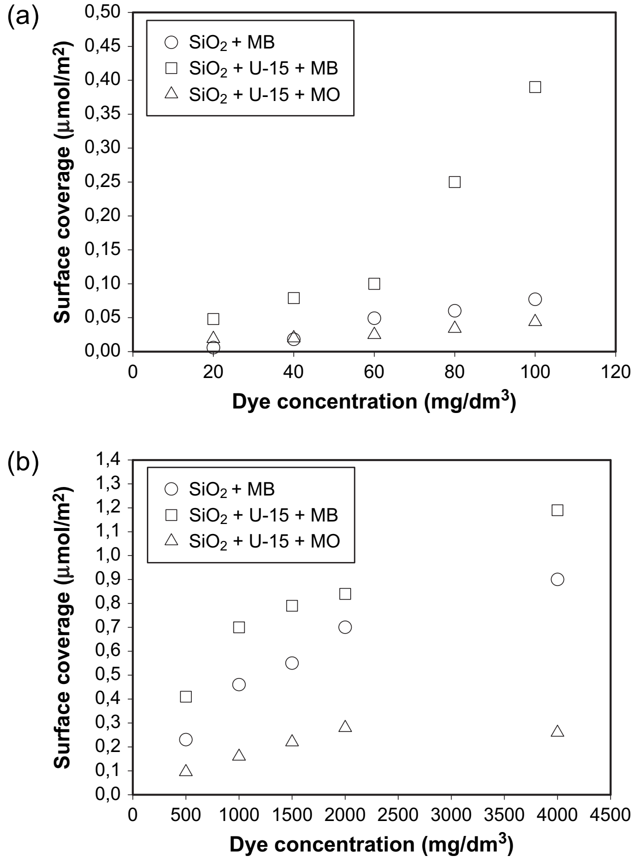


Fig. 1. Relationship between the extent of covering unmodified and modified silica on one hand and concentration of the dye on the other.

3.2. Electrokinetic properties

Colloidal (electrokinetic) properties of silica markedly depend on substances adsorbed at its surface. When adsorbed at the particle surface, even low amounts of a compound may significantly affect density of the surface charge and, thus, zeta potential and stability of the dispersion (or its absence) [22]. Zeta potential represents the parameter which characterises stability of electrostatically stabilised dispersions [23], with the high (positive or negative) zeta potential being typical for stable systems and low zeta potential – for unstable systems.

Isoelectric point (IEP) indicates the pH at which zeta potential is equal 0. At such a pH the value of negative charge equilibrates the positive charge. IEP of silica used to be around pH = 2 but it depends on the type and concentration of electrolyte, type of silica (unmodified–modified) and on specific ion adsorption on silica surface [24]. Close to IEP, dispersive silica systems can be assumed to exhibit the lowest stability.

The relation of zeta potential on pH for the unmodified silica and for the hybrid systems consisting of unmodified silica and Methylene Blue (MB) at 500 and 4000 mg/dm^3 is presented in Fig. 2. For the unmodified silica zeta potential maintained negative values in the entire range of pH. A similar result was obtained for the hybrid systems: SiO_2 + 500 mg/dm^3 MB and SiO_2 + 4000 mg/dm^3 MB. In none of the cases the measurements permitted to define accurately IEP. Nevertheless, shape of the curves suggested that they tended to reach IEP value of 1.45–1.55 for the unmodified silica, 1.55–1.60 for the SiO_2 + 500 mg/dm^3 MB system, 2.50–2.60 for the SiO_2 + 4000 mg/dm^3 MB system. The tendency was noted for the shift of electrokinetic curves toward higher pH values with increasing amounts of the applied dye. The most pronounced shift was noted for the system of unmodified silica and Methylene Blue at 4000 mg/dm^3.

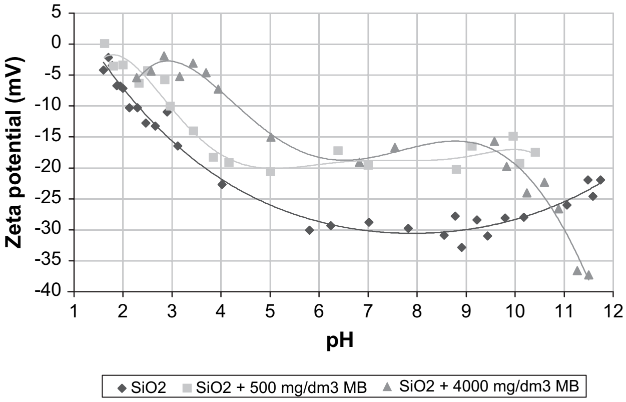


Fig. 2. Relationship between zeta potential and pH (0.001 M NaCl) for the unmodified silica/Methylene Blue hybrid systems.

The relationships between zeta potential and pH for the silica modified with 3 weight parts of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15) and for the hybrid systems of the modified silica/Methylene Blue (MB) at 500 and 4000 mg/dm^{3}of the latter are presented in Fig. 3. In this case, the curve for the modified silica markedly diverged from that for the unmodified silica. Following modification with 3 weight parts of U-15, isoelectric point of the silica amounted to 3.65. At lower pH values, zeta potential acquired a positive value (maximum: +16.23 mV), and at higher pH values it showed a negative value (minimum: −37.34 mV). Isoelectric points of the hybrid systems also diverged from those obtained for the unmodified silica and amounted to 4.25 for SiO_2 + 3 weight parts of U-15 + 500 mg/dm^3 MB and 3.1 for SiO_2 + 3 weight parts of U-15 + 4000 mg/dm^3 MB, respectively.

The so significant shift of isoelectric point toward higher pH values resulted from the strong protonising effect of aminosilane U-15 $-NH_2$ groups. Dissociation of the groups played a very important role in alterations of SiO_2 surface charge. In the case of high density H^+ ions induction of $-NH_3^+$ groups followed resulting in a positive surface charge of the modified silica.

Nevertheless, the shift of electrokinetic curves toward higher pH values with increasing amounts of the applied dye persisted. Similar to the first case, this could be noted best for the system of silica modified with 3 weight parts of U-15 + 4000 mg/dm^3 MB.

In the latter case (Fig. 4) the studies were repeated for the aminosilane-modified silica, but for the formation of hybrid systems C.I. Acid Orange 52 (MO) was applied in the same amounts as in the case of C.I. Basic Blue 9 (MB) (500 and 4000 mg/dm^3). The resulting isoelectric points amounted to 4.65 for SiO_2 + 3 weight parts of U-15 + 500 mg/dm^3 MO and 4.3 for SiO_2 + 3 weight parts of U-15 + 4000 mg/dm^3 MO. The isoelectric curve and isoelectric point for the modified silica were identical to those shown in Fig. 3. As compared to the systems containing Methylene Blue, a slight shift of IEP was noted for the hybrid systems containing Methyl Orange. Analogous to the first two cases, this was best illustrated by the curve for the modified silica with supplementation of Methyl Orange at 4000 mg/dm^3.

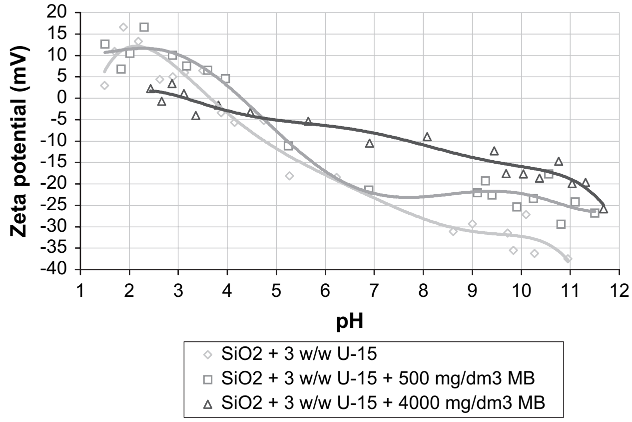


Fig. 3. Relationship between zeta potential and pH (0.001 M NaCl) for the *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane-modified silica/Methylene Blue hybrid systems.

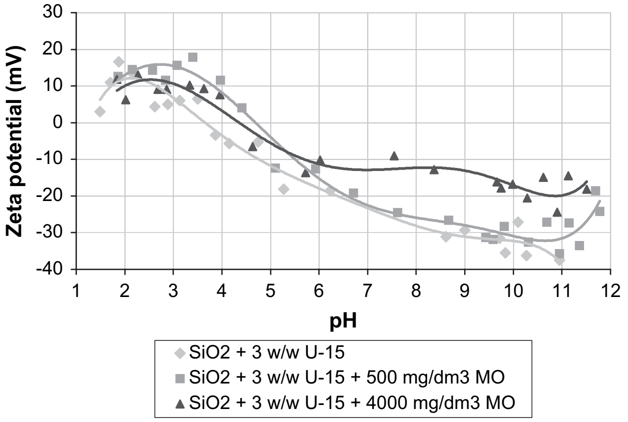


Fig. 4. Relationship between zeta potential and pH (0.001 M NaCl) for the *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane-modified silica/Methyl Orange hybrid systems.

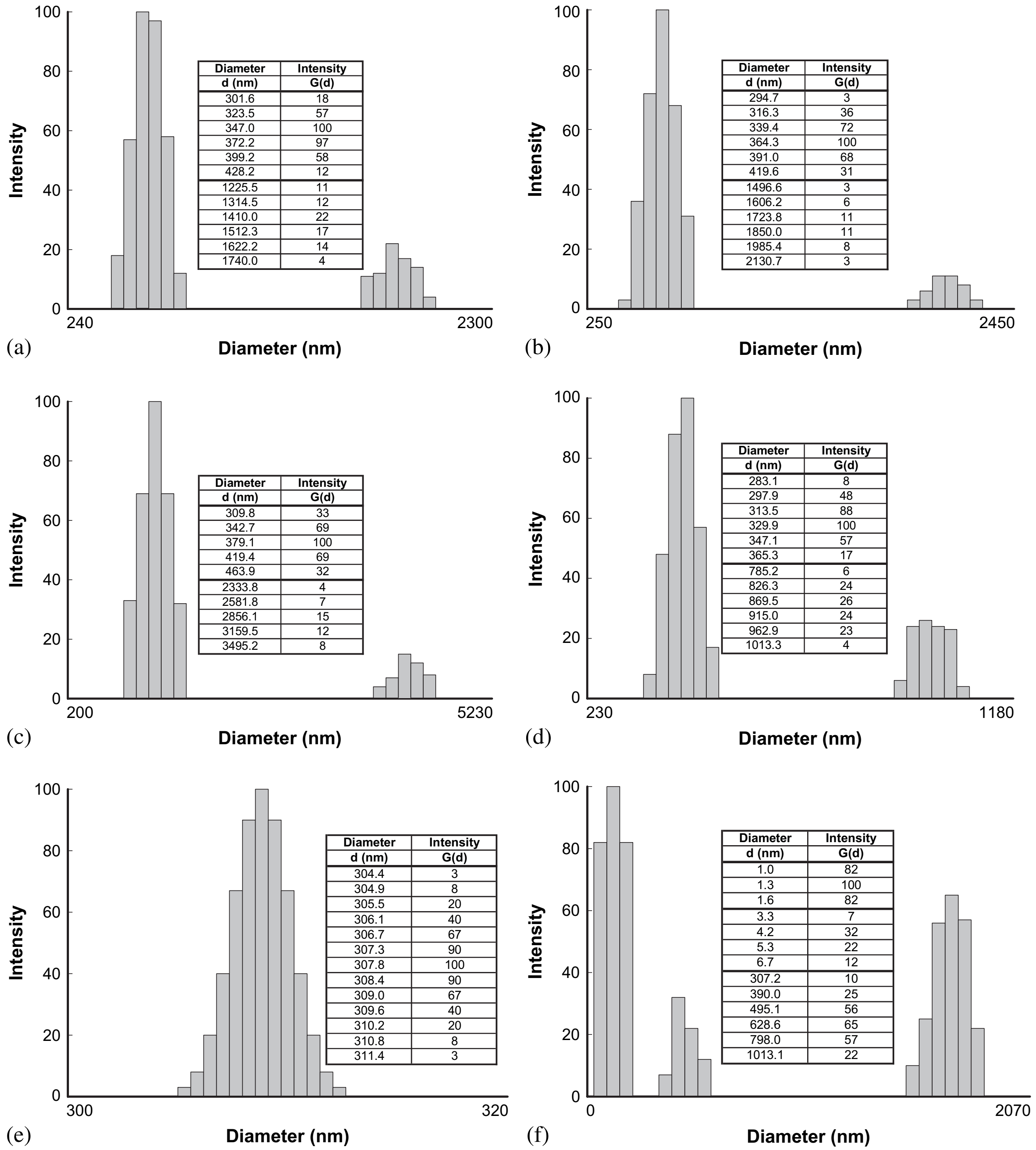
3.3. Dispersive behaviour

Measurements of polydispersity, mean particle diameter and effective particle diameter for the unmodified silica, precipitated in the emulsion system, and for the hybrid systems of unmodified silica/Methylene Blue are presented in Table 1. In turn, multimodal particle size distributions for the above silica systems are shown in Fig. 5.

The particle size distribution (Fig. 5a), reflecting dispersive character of unmodified silica (sample 1), demonstrated the two typical bands. The first band, shows the presence of lower diameters, spanned the range of 302−428 nm, while the other, providing evidence for formation of larger particle clumps (the so called aggregate and agglomerate structures) or for the presence of particles of a higher diameter, fitted the range of 1225−1740 nm. For the unmodified silica, the mean particle diameter was 565 nm, while the effective particle diameter, taking into account the outer surface and shape factors, amounted to 431 nm. Polydispersity, reflecting the scatter of particle sizes, amounted to 0.095, and its relatively low value pointed to the relatively favourable uniform character of the sample.

Particle size distributions for selected hybrids of unmodified silica/Methylene Blue (MB) are exemplified in Fig. 5.

Also, the hybrid system of SiO_2 + 20 mg/dm^3 MB demonstrated the presence of two bands (Fig. 5b). The



(a)

Diameter d (nm)	Intensity G(d)
301.6	18
323.5	57
347.0	100
372.2	97
399.2	58
428.2	12
1225.5	11
1314.5	12
1410.0	22
1512.3	17
1622.2	14
1740.0	4

(b)

Diameter d (nm)	Intensity G(d)
294.7	3
316.3	36
339.4	72
364.3	100
391.0	68
419.6	31
1496.6	3
1606.2	6
1723.8	11
1850.0	11
1985.4	8
2130.7	3

(c)

Diameter d (nm)	Intensity G(d)
309.8	33
342.7	69
379.1	100
419.4	69
463.9	32
2333.8	4
2581.8	7
2856.1	15
3159.5	12
3495.2	8

(d)

Diameter d (nm)	Intensity G(d)
283.1	8
297.9	48
313.5	88
329.9	100
347.1	57
365.3	17
785.2	6
826.3	24
869.5	26
915.0	24
962.9	23
1013.3	4

(e)

Diameter d (nm)	Intensity G(d)
304.4	3
304.9	8
305.5	20
306.1	40
306.7	67
307.3	90
307.8	100
308.4	90
309.0	67
309.6	40
310.2	20
310.8	8
311.4	3

(f)

Diameter d (nm)	Intensity G(d)
1.0	82
1.3	100
1.6	82
3.3	7
4.2	32
5.3	22
6.7	12
307.2	10
390.0	25
495.1	56
628.6	65
798.0	57
1013.1	22

Fig. 5. Particle size distribution (a) for unmodified silica and unmodified silica/Methylene Blue hybrid systems: (b) SiO_2 + 20 mg/dm^3 MB; (c) SiO_2 + 40 mg/dm^3 MB; (d) SiO_2 + 100 mg/dm^3 MB; (e) SiO_2 + 500 mg/dm^3 MB; (f) SiO_2 + 4000 mg/dm^3 MB.

first band corresponded to particles of 295–420 nm in diameter. Maximum intensity of 100 corresponded to particles of 364 nm in diameter. On the other hand, the other band fitted the diameter range of 1497–2131 nm. Maximum intensity of 11 corresponded to particles of 1724–1850 nm in diameter. Mean diameter of the particles, effective particle diameter and polydispersity reached lower values than those for the unmodified silica and amounted, respectively, to 536 nm, 416 nm and 0.044.

Increase in the amount of adsorbed organic dye (to 40 mg/dm^3) resulted in particular in augmented mean particle diameter (714 nm) and augmented polydispersity (0.142), as compared to the unmodified silica. In the particle size distribution (Fig. 5c) again two bands could be observed, the second of which corresponded to markedly larger agglomerates (2334–3495 nm) but the band showed low maximum intensity (15).

Particle size distributions for unmodified silica with the surface-adsorbed Methylene Blue at 60 mg/dm^3

(sample 4) and 80 mg/dm^3 (sample 5) demonstrated that hybrids could be obtained which manifested closely similar particle sizes as well as similar particle size distributions. On the other hand, the hybrid system of SiO_2 + 100 mg/dm^3 MB manifested a relatively low mean particle diameter of 308 nm, relatively low effective particle diameter (391 nm) and low polydispersity (0.034) – Table 1. In the particle size distribution (Fig. 5d) the band of higher intensity fitted the range of 283–365 nm (maximum intensity of 100 corresponded to particles of 330 nm in diameter). Another band of moderate intensity (maximum intensity of 26 corresponded to particles of 869 nm in diameter) represented particles of 785–1113 nm in diameter.

A completely distinct dispersive character was observed when Methylene Blue, at the concentration of 500 mg/dm^3 or 1000 mg/dm^3, was adsorbed on the surface of unmodified silicon dioxide. In either case, hybrids of a monodisperse character resulted, as proved by respective polydispersities, which amounted to 0.005. In the particle size distribution (Fig. 5e) a band was present which spanned the range of 304–311 nm. Maximum intensity of 100 corresponded to particles of 308 nm order in diameter. In turn, for the hybrid of SiO_2 + 1000 mg/dm^3 MB the particles were present in the range of 288–293 nm, and maximum intensity of 100 corresponded to the particle diameter of 291 nm.

Higher amounts of the adsorbed dye (sample 9) also resulted in production of a pigment with a uniform and a relatively low particle size (277 nm).

The pigment obtained by adsorption of 2000 mg/dm^3 MB on the surface of unmodified silicon dioxide demonstrated particle distribution in three bands. The first band of the lowest intensity (2) provided evidence for the presence of particles of 35 nm in diameter, the second band showed also a low intensity and corresponded to particles of 119–147 nm in diameter. On the other hand, the third band reached maximum intensity of 100 for the particles of 412 nm in diameter and spanned the range of 345–561 nm. The deteriorated homogeneity of particles was reflected by the relatively high polydispersity of 0.210.

The use of maximum concentration of the dye for adsorption on the silica (4000 mg/dm^3) induced extensive alterations in the particle size distribution (Fig. 5f), as compared to adsorption at lower dye concentrations. In the particle size distribution the maximum intensity band could be noted in the range of 1.0–1.6 nm and a band in the diameter range of 3.3–6.7 nm. The bands provided proof for the presence of an unadsorbed organic dye. The third band of maximum intensity of 65 fitted the diameter range of 307–1113 nm and reflected the presence of the obtained hybrid. The mean particle diameter showed the lowest value among all the studied systems of unmodified silica/C.I. Basic Blue 9 while polydispersity reached the highest value of 1.276. However, the low value of mean particle diameter in the hybrid did not indicate excellent parameters of the pigment since it resulted largely from diameters of colloidal particles of the unadsorbed dye.

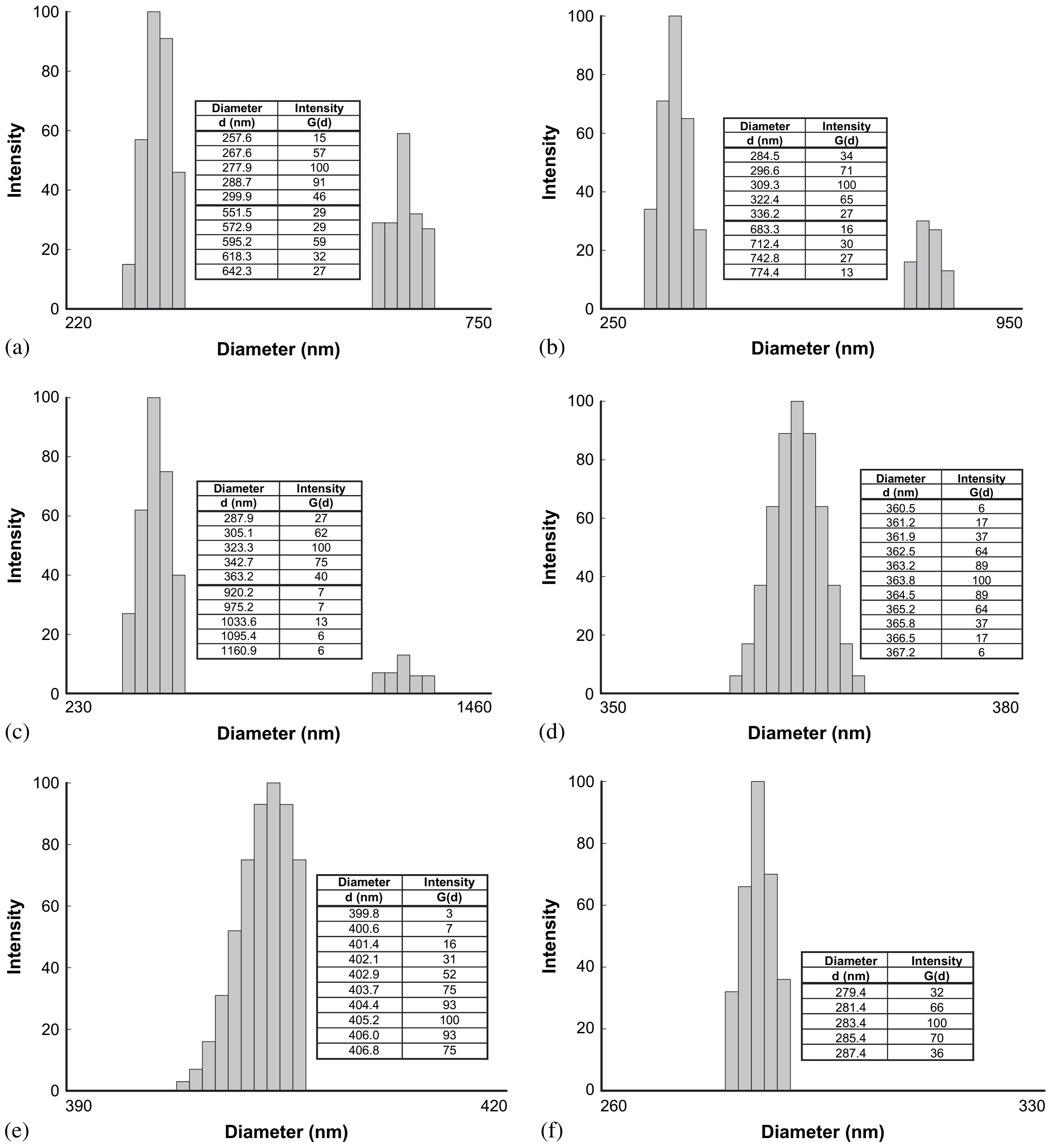
Another significant element of present studies involved evaluation of the effect of silica surface modification using 3 weight parts of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane on its dispersive character and on selective adsorption of organic dyes. In numerous studies [11,13,25–27], the aminosilane-modified silica was found to provide a potentially advantageous carrier of the substances.

The values of polydispersity, mean particle diameter and effective particle diameter for the modified silica/C.I. Basic Blue 9 hybrid systems are shown in Table 2. The respective particle size distributions for the formed hybrid systems are illustrated in Fig. 6.

Silica modified with 3 weight parts of U-15 aminosilane demonstrated mean particle diameter and effective particle diameter slightly higher than those for the unmodified silica. The respective particle size distribution demonstrated two bands. The first band of

Table 2
Dispersive and chemical properties of aminosilane-grafted SiO_2/C.I. Basic Blue 9 hybrid

Sample	Hybrid content	Dispersion evaluation			Elemental analysis		
		Mean particle diameter (nm)	Polydispersity	Effective particle diameter (nm)	Content (%)		
					C	N	S
12	SiO_2 + 3 w/w U-15	640	0.062	531	9.806	0.350	–
13	SiO_2 + 3 w/w U-15 + 20 mg/dm^3 MB	396	0.043	358	9.917	0.386	–
14	SiO_2 + 3 w/w U-15 + 40 mg/dm^3 MB	380	0.018	331	9.986	0.387	–
15	SiO_2 + 3 w/w U-15 + 60 mg/dm^3 MB	402	0.040	362	10.051	0.388	0.059
16	SiO_2 + 3 w/w U-15 + 80 mg/dm^3 MB	405	0.012	364	10.382	0.389	0.063
17	SiO_2 + 3 w/w U-15 + 100 mg/dm^3 MB	376	0.065	341	10.691	0.394	0.080
18	SiO_2 + 3 w/w U-15 + 500 mg/dm^3 MB	364	0.005	394	10.693	0.394	0.091
19	SiO_2 + 3 w/w U-15 + 1000 mg/dm^3 MB	376	0.034	401	11.380	0.660	0.234
20	SiO_2 + 3 w/w U-15 + 1500 mg/dm^3 MB	405	0.021	450	11.581	0.745	0.316
21	SiO_2 + 3 w/w U-15 + 2000 mg/dm^3 MB	1066	0.294	595	11.675	0.848	0.389
22	SiO_2 + 3 w/w U-15 + 4000 mg/dm^3 MB	283	0.687	244	12.416	0.997	0.681



(a)

Diameter d (nm)	Intensity G(d)
257.6	15
267.6	57
277.9	100
288.7	91
299.9	46
551.5	29
572.9	29
595.2	59
618.3	32
642.3	27

(b)

Diameter d (nm)	Intensity G(d)
284.5	34
296.6	71
309.3	100
322.4	65
336.2	27
683.3	16
712.4	30
742.8	27
774.4	13

(c)

Diameter d (nm)	Intensity G(d)
287.9	27
305.1	62
323.3	100
342.7	75
363.2	40
920.2	7
975.2	7
1033.6	13
1095.4	6
1160.9	6

(d)

Diameter d (nm)	Intensity G(d)
360.5	6
361.2	17
361.9	37
362.5	64
363.2	89
363.8	100
364.5	89
365.2	64
365.8	37
366.5	17
367.2	6

(e)

Diameter d (nm)	Intensity G(d)
399.8	3
400.6	7
401.4	16
402.1	31
402.9	52
403.7	75
404.4	93
405.2	100
406.0	93
406.8	75

(f)

Diameter d (nm)	Intensity G(d)
279.4	32
281.4	66
283.4	100
285.4	70
287.4	36

Fig. 6. Particle size distributions for the hybrid systems of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane-modified silica/Methylene Blue: (a) SiO_2 + 3 w/w U-15 + 20 mg/dm^3 MB; (b) SiO_2 + 3 w/w U-15 + 60 mg/dm^3 MB; (c) SiO_2 + 3 w/w U-15 + 80 mg/dm^3 MB; (d) SiO_2 + 3 w/w U-15 + 500 mg/dm^3 MB; (e) SiO_2 + 3 w/w U-15 + 1500 mg/dm^3 MB; (f) SiO_2 + 3 w/w U-15 + 4000 mg/dm^3 MB.

maximum intensity provided evidence for the presence of particles of 390–487 nm in diameter (maximum intensity of 100 corresponded to particles of 435 nm in diameter). The other band fitted the range of 1253–1481 nm.

Adsorption of Methylene Blue at 20 mg/dm^3 on the surface of the modified silica resulted in an evident decrease in particle size (Fig. 6a). In this case, the more intense band contained particles of 258–300 nm in diameter while the less intense band indicated the presence of particles of 551–642 nm in diameter. In the sample, mean particle diameter and polydispersity amounted to 396 nm and 0.043, respectively.

Adsorption of C.I. Basic Blue 9 dye at 40 mg/dm^3 was followed only by an increase in diameters of the aggregates or agglomerates, which reached values of 1462–1890 nm.

The particle size distributions presented in Fig. 6b and c demonstrated an almost identical shape. They provided proof for the presence of particles in two ranges of diameters. Mean diameter of their particles amounted to around 400 nm.

Also the produced hybrid (sample 17) manifested the presence of particles in two ranges of diameters. The two bands in the particle size distribution showed an almost identical intensity and spanned the ranges of 223–453 nm and of 468–536 nm, respectively.

Monodisperse character of the formed pigments was obtained following adsorption of Methylene Blue on aminosilane-modified silica at 500, 1000, 1500, and 4000 mg/dm^3 (for example, Fig. 6d and e).

Adsorption of the dye at its highest concentration led to formation of a SiO_2/organic dye hybrid of an almost twofold lower particle diameter than that of aminosilane-modified silica. Moreover, the mean particle diameter of 283 nm and the effective diameter of 244 nm were the lowest values noted in the study for the examined colloidal systems (Fig. 6f).

Dispersive properties of the modified silica/Methyl Orange hybrid systems are presented in Table 3 and Fig. 7.

In the particle size distributions (Fig. 7a–d) two typical bands were observed. In every case the first band showed maximum intensity and spanned the closely related range of diameters (around 260–400 nm). The other band was definitely less intense and characterised aggregate and agglomerate forms of the formed clumps.

The sample 27, resulting from adsorption of 100 mg Methyl Orange/dm^3 on the aminosilane-modified silica, demonstrated three ranges of particle manifestation. The first band included particles of 221–417 nm in size (maximum intensity of 100 corresponded to the particles of 324 nm in size). The two other bands reflected the presence of very large agglomerates. They reached diameters of 4109–7425 nm but were present in trace amounts only. The mean particle diameter was 530 nm and the polydispersity amounted to 0.054.

The subsequent hybrid formed (sample 29) showed an almost identical dispersive character to that of the hybrid obtained with the fivefold lower amount of the adsorbed C.I. Acid Orange 52 dye (Fig. 7e). In this case one band was present of maximum intensity in the range of 228–326 nm and the other of a twofold lower intensity in the range of 1027–1469 nm. In the pigment, mean particle diameter was 585 nm, effective particle diameter was 377 nm, and polydispersity amounted to 0.230.

Adsorption of the C.I. Acid Orange 52 dye at 1500 mg/dm^3 on the modified silicon dioxide resulted in a pigment of a very strong tendency for particle agglomeration. In the particle size distribution (Fig. 7f) three typical bands were seen. The first two of higher intensities represented particles in the range of 211–1088 nm. The third band provided proof for the presence of huge particle accumulations, of 3965–6812 nm in size (maximum intensity of 7 corresponded to the agglomerates of 4923–6113 nm in size). Also the sample 31 manifested the three-modal particle size distribution but in this case the third band, reflecting the presence of agglomerate structures, was more intense (maximum intensity of 34 corresponded to particles of 2122 nm in size) and contained particles of 1686–2996 nm in diameter. In this case, mean particle diameter, polydispersity and affective particle diameter reached the highest values among all the studied pigments formed with the Methyl Orange.

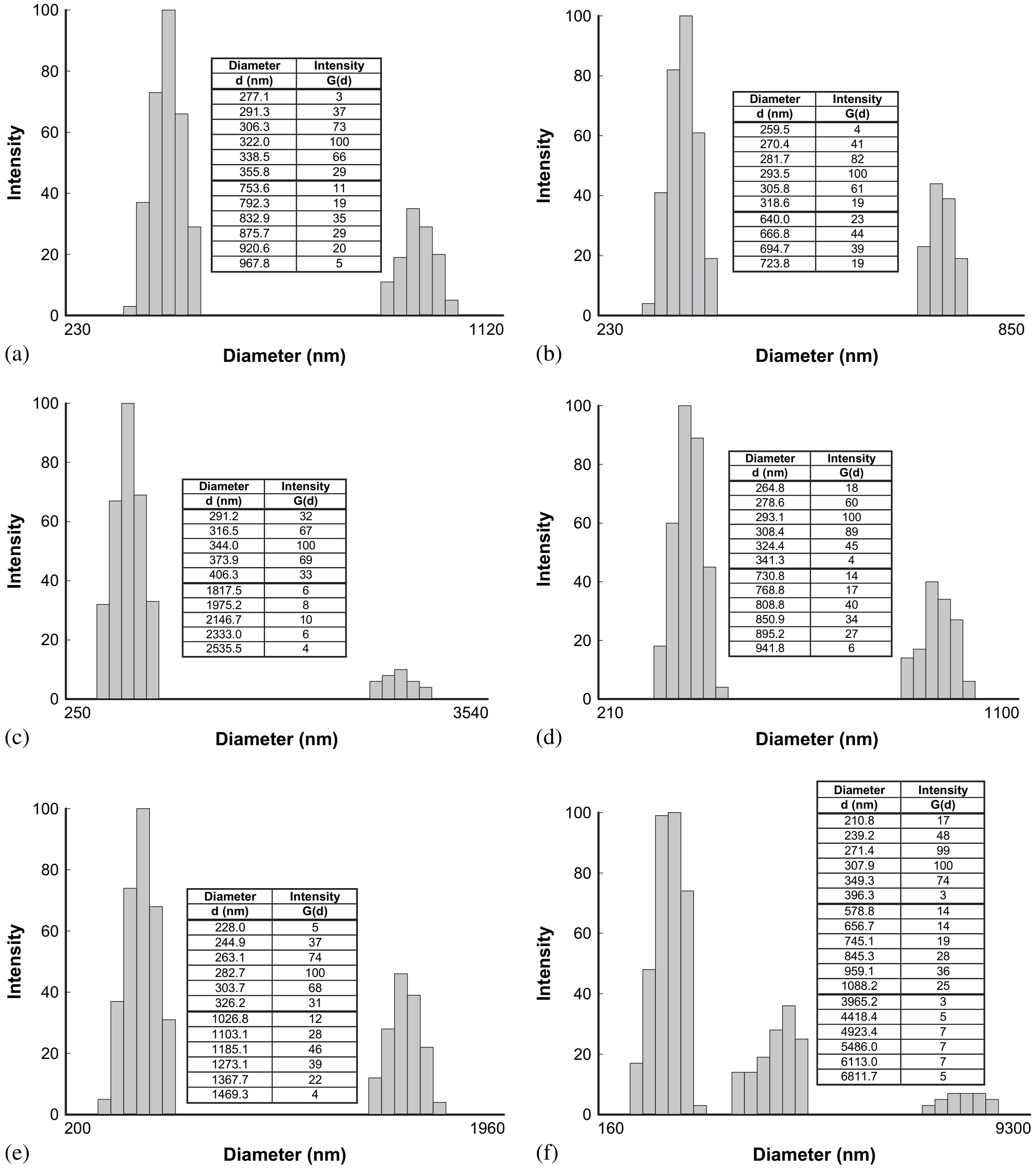
Sample 32 demonstrated the typical dimodal size distribution. The first band was noted in the range of 308–421 nm and the other in the range of 1146–1567 nm. In the pigment, mean particle diameter was 556 nm, effective particle diameter was 427 nm, and polydispersity reached the value of 0.145.

3.4. Colorimetric properties

Colorimetric studies, performed in the CIE $L^*a^*b^*$ system, permitted to obtain data on changes in input of individual colours following adsorption of C.I. Basic Blue 9 on unmodified silica (Table 4), of C.I. Basic Blue 9 on aminosilane-functionalised silica (Table 5), and of

Table 3
Dispersive and chemical properties of aminosilane-grafted SiO_2/C.I. Acid Orange 52 hybrid

Sample	Hybrid content	Dispersion evaluation			Elemental analysis		
		Mean particle diameter (nm)	Polydispersity	Effective particle diameter (nm)	Content (%)		
					C	N	S
23	SiO_2 + 3 w/w U-15 + 20 mg/dm^3 MO	468	0.083	397	9.844	0.352	0.009
24	SiO_2 + 3 w/w U-15 + 40 mg/dm^3 MO	404	0.078	354	9.850	0.353	0.015
25	SiO_2 + 3 w/w U-15 + 60 mg/dm^3 MO	527	0.043	393	9.856	0.354	0.025
26	SiO_2 + 3 w/w U-15 + 80 mg/dm^3 MO	459	0.107	378	9.874	0.355	0.032
27	SiO_2 + 3 w/w U-15 + 100 mg/dm^3 MO	530	0.054	336	9.894	0.356	0.043
28	SiO_2 + 3 w/w U-15 + 500 mg/dm^3 MO	463	0.058	346	9.996	0.360	0.071
29	SiO_2 + 3 w/w U-15 + 1000 mg/dm^3 MO	585	0.230	377	10.117	0.364	0.085
30	SiO_2 + 3 w/w U-15 + 1500 mg/dm^3 MO	785	0.213	388	10.248	0.428	0.090
31	SiO_2 + 3 w/w U-15 + 2000 mg/dm^3 MO	889	0.247	479	10.356	0.498	0.098
32	SiO_2 + 3 w/w U-15 + 4000 mg/dm^3 MO	566	0.145	427	10.332	0.456	0.101



Diameter d (nm)	Intensity G(d)
277.1	3
291.3	37
306.3	73
322.0	100
338.5	66
355.8	29
753.6	11
792.3	19
832.9	35
875.7	29
920.6	20
967.8	5

Diameter d (nm)	Intensity G(d)
259.5	4
270.4	41
281.7	82
293.5	100
305.8	61
318.6	19
640.0	23
666.8	44
694.7	39
723.8	19

Diameter d (nm)	Intensity G(d)
291.2	32
316.5	67
344.0	100
373.9	69
406.3	33
1817.5	6
1975.2	8
2146.7	10
2333.0	6
2535.5	4

Diameter d (nm)	Intensity G(d)
264.8	18
278.6	60
293.1	100
308.4	89
324.4	45
341.3	4
730.8	14
768.8	17
808.8	40
850.9	34
895.2	27
941.8	6

Diameter d (nm)	Intensity G(d)
228.0	5
244.9	37
263.1	74
282.7	100
303.7	68
326.2	31
1026.8	12
1103.1	28
1185.1	46
1273.1	39
1367.7	22
1469.3	4

Diameter d (nm)	Intensity G(d)
210.8	17
239.2	48
271.4	99
307.9	100
349.3	74
396.3	3
578.8	14
656.7	14
745.1	19
845.3	28
959.1	36
1088.2	25
3965.2	3
4418.4	5
4923.4	7
5486.0	7
6113.0	7
6811.7	5

Fig. 7. Particle size distributions for the hybrid systems of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane-modified silica/Methyl Orange: (a) SiO_2 + 3 w/w U-15 + 20 mg/dm^3 MO; (b) SiO_2 + 3 w/w U-15 + 40 mg/dm^3 MO; (c) SiO_2 + 3 w/w U-15 + 60 mg/dm^3 MO; (d) SiO_2 + 3 w/w U-15 + 80 mg/dm^3 MO; (e) SiO_2 + 3 w/w U-15 + 1000 mg/dm^3 MO; (f) SiO_2 + 3 w/w U-15 + 1500 mg/dm^3 MO.

C.I. Acid Orange 52 on the aminosilane-grafted silicon dioxide (Table 6).

In the hybrid system of Methylene Blue/SiO_2 an evidently decreased parameter of lightness (L^*) was noted. Increasing amounts of the adsorbed dye were paralleled also by an evident change in colour (ΔE^*). Nevertheless, in the case of adsorption of C.I. Basic Blue 9 at the concentration of 4000 mg/dm^3, only a slightly lowered parameter of brightness was noted as compared to the twofold lower amount of the adsorbed dye.

In the case of C.I. Basic Blue 9 adsorption on the silica modified with 3 weight parts of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane, very significant alterations could easily be noted in participation of blue colour ($-b^*$) (Table 5). The blue colour was noted already following adsorption of Methylene Blue at the

Table 4
Colorimetric data for the unmodified SiO_2/C.I. Basic Blue 9 hybrid

Sample	Hybrid content	Colorimetric data								
		L^*	a^*	b^*	C^*	h^*	ΔL^*	Δa^*	Δb^*	ΔE^*
1	SiO_2	30.92	−2.25	9.42	9.69	103.46	−62.85	−2.57	6.65	63.26
2	SiO_2 + 20 mg/dm^3 MB	22.95	−2.93	4.79	5.61	121.44	−70.82	−3.24	2.02	70.93
3	SiO_2 + 40 mg/dm^3 MB	21.07	−2.97	2.22	3.71	143.21	−72.69	−3.28	−0.55	72.77
4	SiO_2 + 60 mg/dm^3 MB	18.33	−3.49	1.77	3.92	153.05	−75.43	−3.80	−0.99	75.54
5	SiO_2 + 80 mg/dm^3 MB	17.74	−3.05	−0.73	3.13	193.46	−76.03	−3.36	−3.50	76.19
6	SiO_2 + 100 mg/dm^3 MB	15.68	−2.73	−2.28	3.92	225.91	−78.09	−3.04	−5.58	78.35
7	SiO_2 + 500 mg/dm^3 MB	6.81	0.77	−7.01	7.05	276.24	−86.96	0.45	−9.78	87.51
8	SiO_2 + 1000 mg/dm^3 MB	3.47	1.02	−6.25	6.34	279.28	−90.30	0.71	−9.02	90.75
9	SiO_2 + 1500 mg/dm^3 MB	2.64	1.29	−5.34	5.50	283.61	−91.13	0.98	−8.11	91.50
10	SiO_2 + 2000 mg/dm^3 MB	7.14	6.17	−16.88	17.97	290.08	−86.62	5.86	−19.64	89.02
11	SiO_2 + 4000 mg/dm^3 MB	2.48	1.23	−4.90	5.05	284.11	−91.29	0.92	−7.67	91.61

Table 5
Colorimetric data for aminosilane-grafted SiO_2/C.I. Basic Blue 9 hybrid

Sample	Hybrid content	Colorimetric data								
		L^*	a^*	b^*	C^*	h^*	ΔL^*	Δa^*	Δb^*	ΔE^*
13	SiO_2 + 3 w/w U-15 + 20 mg/dm^3 MB	43.10	−2.58	0.43	2.62	170.63	−50.67	−2.90	−2.34	50.80
14	SiO_2 + 3 w/w U-15 + 40 mg/dm^3 MB	39.84	−2.25	−0.85	2.41	200.73	−53.93	−2.57	−3.62	54.11
15	SiO_2 + 3 w/w U-15 + 60 mg/dm^3 MB	37.02	−1.59	−3.15	3.53	243.16	−56.75	−1.91	−5.92	57.09
16	SiO_2 + 3 w/w U-15 + 80 mg/dm^3 MB	34.45	−1.85	−3.69	4.13	243.30	−59.32	−2.17	−6.45	59.71
17	SiO_2 + 3 w/w U-15 + 100 mg/dm^3 MB	32.46	−1.43	−5.23	5.42	254.76	−61.30	−1.74	−8.00	61.85
18	SiO_2 + 3 w/w U-15 + 500 mg/dm^3 MB	17.85	1.90	−14.96	15.08	277.22	−75.92	1.58	−17.73	77.98
19	SiO_2 + 3 w/w U-15 + 1000 mg/dm^3 MB	12.59	2.23	−14.84	15.00	278.54	−81.18	1.91	−17.60	83.09
20	SiO_2 + 3 w/w U-15 + 1500 mg/dm^3 MB	10.26	3.40	−15.13	15.50	282.65	−83.50	3.08	−17.89	85.46
21	SiO_2 + 3 w/w U-15 + 2000 mg/dm^3 MB	9.94	3.97	−15.42	15.92	284.44	−83.83	3.65	−18.18	85.85
22	SiO_2 + 3 w/w U-15 + 4000 mg/dm^3 MB	4.88	1.83	−10.15	10.31	280.25	−88.89	1.52	−12.92	89.84

Table 6
Colorimetric data for aminosilane-grafted SiO_2/C.I. Acid Orange 52 hybrid

Sample	Hybrid content	Colorimetric data								
		L^*	a^*	b^*	C^*	h^*	ΔL^*	Δa^*	Δb^*	ΔE^*
23	SiO_2 + 3 w/w U-15 + 20 mg/dm^3 MO	30.52	−2.35	16.94	17.10	97.9	−63.29	−2.57	14.17	64.91
24	SiO_2 + 3 w/w U-15 + 40 mg/dm^3 MO	29.30	−1.45	17.96	18.02	94.62	−64.51	−1.67	15.19	66.30
25	SiO_2 + 3 w/w U-15 + 60 mg/dm^3 MO	29.70	−1.57	18.15	18.22	94.95	−64.12	−1.79	15.38	65.96
26	SiO_2 + 3 w/w U-15 + 80 mg/dm^3 MO	29.96	−1.57	18.78	18.84	94.77	−63.86	−1.79	16.01	65.86
27	SiO_2 + 3 w/w U-15 + 100 mg/dm^3 MO	29.77	−1.03	21.54	21.57	92.75	−64.05	−1.25	18.77	66.75
28	SiO_2 + 3 w/w U-15 + 500 mg/dm^3 MO	29.60	−0.87	22.95	22.96	92.18	−64.22	−1.09	20.17	67.32
29	SiO_2 + 3 w/w U-15 + 1000 mg/dm^3 MO	28.88	0.77	26.63	26.64	88.35	−64.94	0.55	23.86	69.19
30	SiO_2 + 3 w/w U-15 + 1500 mg/dm^3 MO	28.61	1.88	29.14	29.20	86.32	−65.21	1.66	26.42	70.36
31	SiO_2 + 3 w/w U-15 + 2000 mg/dm^3 MO	27.68	3.32	31.25	31.42	83.94	−66.14	3.10	28.64	72.08
32	SiO_2 + 3 w/w U-15 + 4000 mg/dm^3 MO	23.96	3.31	29.50	29.69	83.61	−69.86	3.09	26.90	74.86

concentration of 40 mg/dm^3. Following adsorption of the dye on the unmodified silica, evident participation of the blue colour ($-b^*$) could not be noted until the dye reached concentration of 80 mg/dm^3.

Studies on adsorption of C.I. Acid Orange 52 on aminosilane-grafted silica were paralleled by an evident change in participation of green ($-a^*$) and yellow ($+b^*$) colours. With increasing concentration of Methyl Orange an evident saturation with the red ($+a^*$) and yellow ($+b^*$) colour was noted. The share of yellow colour doubled with the applied MO concentrations rising from 20 to 4000 mg/dm^3. Moreover, chrome intensity (C^*) also doubled.

Similar to the hybrids obtained following adsorption of C.I. Basic Blue 9 (samples 11 and 22), the hybrid produced by adsorption of C.I. Acid Orange 52 at the concentration of 4000 mg/dm^3 showed no intense colour, as proven by the results of colorimetric studies, as compared to results of adsorption of the organic dyes at the concentration of 2000 mg/dm^3. This probably reflected saturation of active adsorptive sites on the silica carriers, responsible for efficiency of the chemical adsorption. Also, adsorption of C.I. Basic Blue 9 or C.I. Acid Orange 52 at the concentration of 2000 mg/dm^3 on either unmodified or modified silica seemed to result in maximum colour intensity.

4. Conclusions

In the conducted studies on dye adsorption, application of aminosilane-functionalised silica as an adsorbent was found to increase efficiency of C.I. Basic Blue 9 adsorption as compared to the unmodified silica. Electrokinetic studies demonstrated that zeta potential of unmodified silica showed negative values in the entire range of pH. Increasing concentrations of adsorbed MB were accompanied by a shift of the electrokinetic curves toward higher pH values. Significant shifts in isoelectric point for the aminosilane-grafted silica resulted from a strong protonising effect of amine groups. The produced pigments demonstrated a favourable particle dispersion and a restricted tendency to form agglomerates. This was confirmed by most particle size distributions. Colorimetric studies allowed for an objective evaluation of colour of the formed pigments. The obtained results provide the potential to monitor adsorbate concentration in order to obtain hybrid pigments of appropriate colorimetric properties. The obtained pigments, particularly following adsorption of dyes at their higher concentration, exhibited high intensity of the colour and its optimum hue.

Acknowledgements

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