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The preparation of pigment composites by adsorption of C.I. Mordant Red 11 and 9-aminoacridine on both unmodified and aminosilane-grafted silica supports

Teofil Jesionowski*, Agnieszka Przybylska, Beata Kurc, Filip Ciesielczyk

Poznan University of Technology, Institute of Chemical Technology and Engineering, M. Sklodowskiej-Curie 2 Sq., 60-965 Poznan, Poland

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ABSTRACT

Pigment composites were obtained by adsorption of 9-aminoacridine and C.I. Mordant Red 11 onto silica supports which were both unmodified and also modified with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane. The silica supports and pigment composites were characterised using particle size and polydispersity index, particle morphology and the presence of agglomerates, as well as sedimentation profile, water wettability and colorimetric parameters. The extent of silica surface coverage with each dye was determined on the basis of elemental analysis. The presence of functional groups on the silica support and the pigment composites was confirmed using FT-IR.

1. Introduction

Organic pigments are extensively used for the production of coatings, inks, polymer composites and colour filters [1] for various electronic and communication applications, owing to their attractive features such as high photosensitivity, wide colour gamut, brilliance, colour strength and transparency. However, their limited hiding power, poor dispersion ability and poor weathering durability limit their use for some applications. Many methods have been explored to resolve the above problems; for example, Lelu et al. [2] encapsulated C.I. Pigment Blue 15 into polystyrene latex particles using microemulsion polymerisation to improve the pigment's dispersion ability in aqueous systems. Moreover the crystalline phase destruction of C.I. Vat Blue 4 and C.I. Pigment Blue 60 leads to improved morphological-dispersive and pigmentation properties [3]. Krysztafkiewicz and Jesionowski described methods for hybrid pigment preparation using inorganic supports modified with silane coupling agents [4]; the hybrid pigments displayed high colour stability. Organic pigments can also applied directly onto silica film, thereby functioning as a protective shell, using a water glass process to improve UV characteristics, stability and heat resistance [4,5]. Recently, organic pigments prepared using colloidal silica and titania as supports have been obtained using a multistep layer-by-layer, self assembly technique [6]. Both natural and synthetic inorganic pigments produced as fine powders are an integral part of many decorative and protective coatings and are used for coloration of many materials, including glazes, ceramics and porcelain enamels [7–9].

Anthraquinones are important natural compounds that enjoy usage in a diverse array of applications, including medicine [10], dyes and colorants [11], the synthesis of hydrogen peroxide [12], analytical reagents and indicators [13]. One of the best known anthraquinones, C.I. Mordant Red 11, can be isolated from plants and displays a marked ability to chelate ions such as calcium, zinc, magnesium and copper. C.I. Mordant Red 11 has been extensively employed since ancient times for dyeing textiles [14]. The adsorption of C.I. Mordant Red 11 on montmorillonites [15], mesoporous silica and hybrid gels as well as on other adsorbents [16,17] has been studied.

Hydroxyanthraquinones have attracted much attention because of their photoactivity [14], their colour depending on the position and number of hydroxyl substituents [18]. In particular, dihydroxyquinones enjoy much use as pharmaceutically active and biologically relevant chromophores. In addition, many dihydroxyquinones have been used as analytical tools for the determination of metals and in electrochemistry [19]. The fluorescent and water-soluble C.I.

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* Corresponding author. Tel.: +48 61 665 37 20; fax: +48 61 665 36 49.
E-mail address: teofil.jesionowski@put.poznan.pl (T. Jesionowski).

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Mordant Red 11 (1,2-dihydroxyanthraquinone), is the most important constituent of the dye lake, madder, which is a pigment precipitated onto an inert inorganic substrate ($Al_2O_3*nH_2O$) [18], and in which form, the dye has been extensively used since ancient times for dyeing textiles; nowadays, C.I. Mordant Red 11 is used in artist paints as synthetic madder [19]. As a biologically active molecule, C.I. Mordant Red 11 displays remarkable antigenotoxic activity, as it is an inhibitor of the human recombinant cytochrome P450 isozyme, as are other anthraquininoid dyes; as such, C.I. Mordant Red 11 as a component of food is an anticarcinogen [20].

9-Aminoacridine (9-AH) is an antibacterial, mutagenic [21], antitumour drug [22] that has been proposed as a specific fluorescent probe capable of wounding the active centre of GB (guanidinobenzoatases). Indeed, the staining of histopathological sections with 9-AH has been used to locate malignant cells in many tumour tissues [23].

The aim of this work was to characterise pigment composites produced by the adsorption of 9-aminoacridine and C.I. Mordant Red 11 on both unmodified and modified silica supports.

2. Experimental

2.1. Methods of obtaining silica support

The first step towards obtaining silica support was to prepare two emulsions. The first, referred to as alkaline one (E1), was composed of the organic phase (cyclohexane, POCh SA) in which nonylphenylpolyoxyethyleneglycol ethers – NP3 and NP6 (PCC ROKITA SA) were dissolved in appropriate amount. The 20% sodium silicate solution (VITROSILICON SA) was also introduced. The other emulsion, referred to as acidic one (E2), was composed of cyclohexane and appropriate amount of NP3 and NP6 ethers and a fixed volume of a 5% solution of hydrochloric acid. The emulsions were prepared by dissolving the weighted portions of the non-ionic surfactants in cyclohexane. Both emulsions were homogenised. At first E2 was homogenised for 20 min at the rate of 8800 rpm, then it was placed in the reactor QVF MiniPlant Pilot-Tec of 10 dm^3 in capacity and continuously stirred at 760 rpm. In the same conditions E1 was homogenised and introduced into the reactor (filled with E2) in doses with the help of a peristaltic pump (Ismatec ISM 828) at the rate of 20 cm^3/min.

The white silica precipitate obtained in the emulsion system was subjected to destabilisation at 80 °C in order to separate the organic phase from the inorganic one. The sample obtained was filtered off under reduced pressure. The filtration disc obtained was washed a few times with hot water and methanol to remove the possible residues of surfactants. The organic solutions were recovered by distillation. The moisture was removed from the silica precipitate by spray drying in a GeoNiro A/S dryer.

2.2. Silica functionalisation

The silica surface functionalisation process was performed in a reactor of 0.5 dm^3 in capacity to which 20 g of silica and a solution of the modifying compound were introduced. The modifying compound was *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane in the amount of 3 wt./wt. prepared in water/methanol mixture as a solvent. The method of modification has been described in detail in [24].

2.3. Pigment composites preparation

Two dyes were used: C.I. Mordant Red 11 (acidic dye) and 9-aminoacridine (basic dye), their characteristic is presented in Table 1.

A portion of 7.5 g of unmodified or modified silica support was placed in a flask of 300 cm^3 in capacity, then 250 cm^3 of a solution of a given dye at a selected concentration (20, 40, 60, 80, 100, 500, 1000, 1500, 2000 and 3000 mg/dm^3) was introduced. The solvent used for both dyes was ethanol. The suspension obtained was mixed for 2 h by a magnetic stirrer IKAMAG R05 made by IKA Werke GmbH. The pigment composite obtained was filtered under reduced pressure, while the washed out precipitate was dried in a stationary dryer for 24 h at 105 °C. In the filtrate the concentration of the unadsorbed dye was determined by absorbency measurements using SPEKOL 1200 spectrophotometer made by Analytik Jena.

2.4. Dye elution from the silica support surface

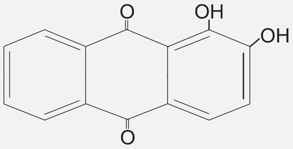
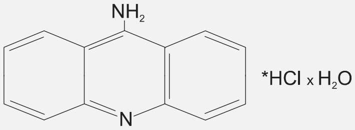
The stability of the pigment composites was evaluated by elution tests. To a conical flask of 200 cm^3 in capacity, containing 20 cm^3 of ethanol, 0.1 g of the pigment was added. The suspension obtained was stirred with a magnetic stirrer IKAMAG R05 made by IKA Werke GmbH for 1 h at room temperature (25 °C). Then the suspension was filtered off under reduced pressure and the concentration of the dye in the filtrate was determined by absorbency measurements using SPEKOL 1200 spectrophotometer.

2.5. Physico-chemical evaluations

The silicas precipitated and the pigment composites obtained were subjected to dispersion study. The particle size distributions were evaluated by Zetasizer Nano ZS and Mastersizer 2000, both made by Malvern Instruments Ltd. The first operates on the basis of non-invasive back scattering (NIBS), while the second – on the basis of laser diffraction. From the particle size distributions it was possible to determine polydispersity, a parameter characterising the homogeneity of the product studied. With the help of Zetasizer Nano ZS it was also possible to measure 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). With the use of a scanning electron microscope (SEM, Zeiss VO40), the morphology and microstructure of the silicas precipitated and randomly chosen pigment composites were characterised. The SEM images permit estimation of the degree of dispersion, structure of individual particles and the tendency to aggregation or agglomeration. Specific surface area of the products obtained was estimated by the low-temperature nitrogen adsorption (at 77 K) on ASAP 2020 made by Micromeritics Instruments Co. and with the use of the BET isotherm equation.

The degree of modification was measured by a spectrophotometer FT-IR EQUINOX 55 made by Bruker. The silica supports and the pigment composites obtained in the form of suspensions in carbon tetrachloride were subjected to IR analysis. Carbon tetrachloride shows small IR absorption in the range of the samples absorption. Reliable results of this method depend on the choice of proper concentration of the suspension and its high stability in CCl_4. The optimum concentration of the suspension of the products studied was found to be 4%. To estimate the hydrophilic/hydrophobic character of the product surface, its wettability with water and the sedimentation profiles in water were determined. The measurements were carried out with a tensiometer K100 (Krüss) with appropriate accessories. Chemical composition of the silicas and pigment composites was analysed using an instrument Elementar, model Vario EL III, and on the basis of the results a degree of silica coverage with a given dye was estimated. The colour of the pigment composites was measured using an SPECOBS 4000 (YETI Technische Instrumente GmbH) colorimeter.

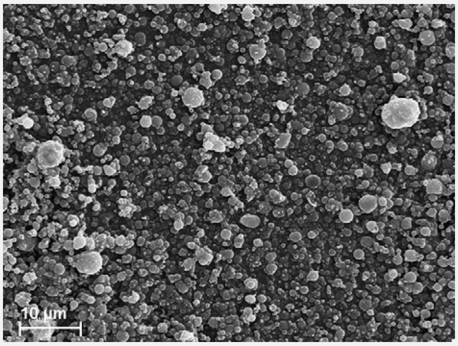
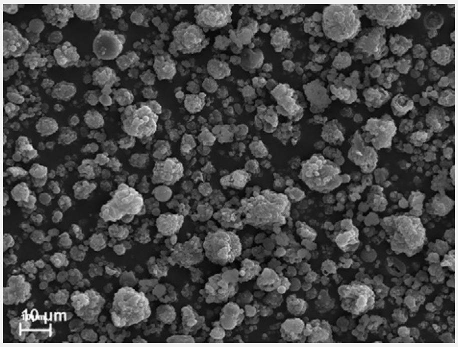
Table 1
Characterisation of the dyes used.

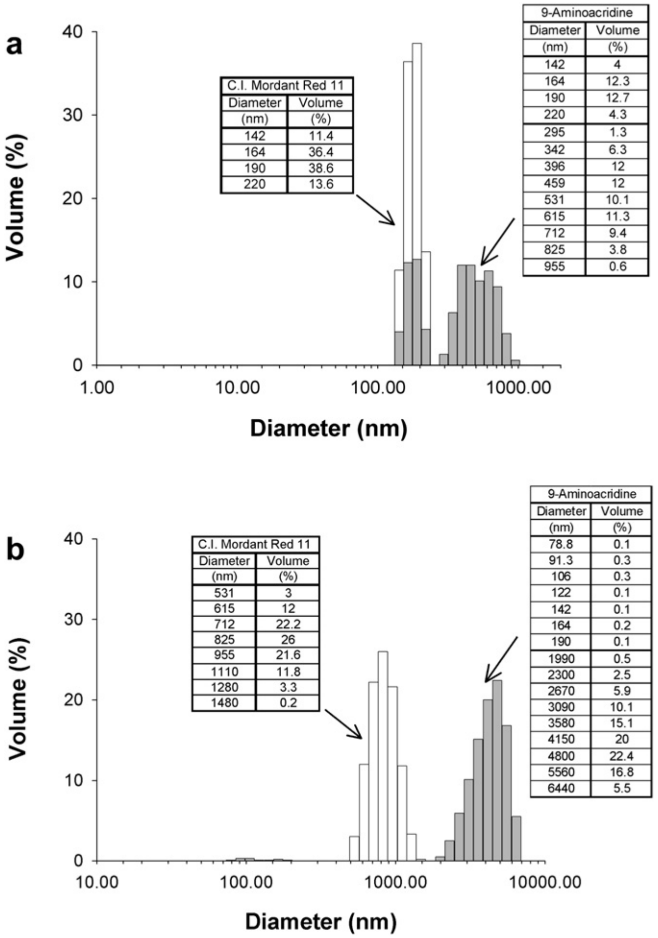
Dye	Structure	Formula	Molecular weight (g/mol)	λ_{max} (nm)
C.I. Mordant Red 11 (Alizarin)		$C_{14}H_8O_4$	240	464
9-Aminoacridine (9-AH)		$C_{13}H_{10}N_2 \cdot HCl \cdot xH_2O$	231	400

3. Results and discussion

At first the dispersion and morphology of silica support unmodified or modified with 3 wt./wt. of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane were estimated. The choice of the modifying agent was made on the basis of our earlier study. The amine groups from silane facilitate formation of a stable chemical bond with the dyes adsorbed [25,26]. Moreover, functionalisation of the inorganic support (e.g. SiO_2–TiO_2) with aminosilane considerably enhances the yield of adsorption. According to the dispersion dates (Table 2), the modification of silica resulted in increased of mean diameter of the particles *D*[4,3] (for unmodified silica $D = 7.540$ μm, while after modification $D = 13.658$ μm). The modification of silica also led to increased volume contribution of secondary agglomerates. Moreover a significant increase in the particle sizes in the diagram showing the volume contribution of particles of a given diameter was observed, manifested by the appearance of the third band corresponding to the particle size range 3090 ÷ 6440 nm. The polydispersity index of the modified silica is 0.156, while that of the unmodified one is 0.061. In both

Table 2
Dispersive and morphological properties of silica support unmodified and modified with 3 wt./wt. of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane.

Silica support type	Particle size distribution (nm) from Zetasizer Nano ZS		PdI	Diameter D[4,3] from Masersizer 2000 (μm)	SEM microphotograph
	by intensity	by volume			
Unmodified	91 ÷ 164 2300 ÷ 5560	1110 ÷ 3090	0.061	7.540	
Modified	68 ÷ 79 122 ÷ 142 1990 ÷ 5560	59 ÷ 79 1720 ÷ 2670 3090 ÷ 6440	0.156	13.658	



a

C.I. Mordant Red 11	
Diameter (nm)	Volume (%)
142	11.4
164	36.4
190	38.6
220	13.6

9-Aminoacridine	
Diameter (nm)	Volume (%)
142	4
164	12.3
190	12.7
220	4.3
295	1.3
342	6.3
396	12
459	12
531	10.1
615	11.3
712	9.4
825	3.8
955	0.6

b

C.I. Mordant Red 11	
Diameter (nm)	Volume (%)
531	3
615	12
712	22.2
825	26
955	21.6
1110	11.8
1280	3.3
1480	0.2

9-Aminoacridine	
Diameter (nm)	Volume (%)
78.8	0.1
91.3	0.3
106	0.3
122	0.1
142	0.1
164	0.2
190	0.1
1990	0.5
2300	2.5
2670	5.9
3090	10.1
3580	15.1
4150	20
4800	22.4
5560	16.8
6440	5.5

Fig. 1. Particle size distributions of the pigment composites obtained as a result of adsorption of C.I. Mordant Red 11 or 9-aminoacridine in the concentration of 100 mg/dm^3 on (a) unmodified SiO_2 and (b) aminosilane-modified silica support.

unmodified and modified silicas the particles were found to show a tendency towards formation of secondary agglomerates and were roughly of spherical shape. The homogeneity of the modified silica was slightly poorer as its particles show a greater tendency to agglomerate (SEM image confirms the presence of agglomerates structures, Table 2).

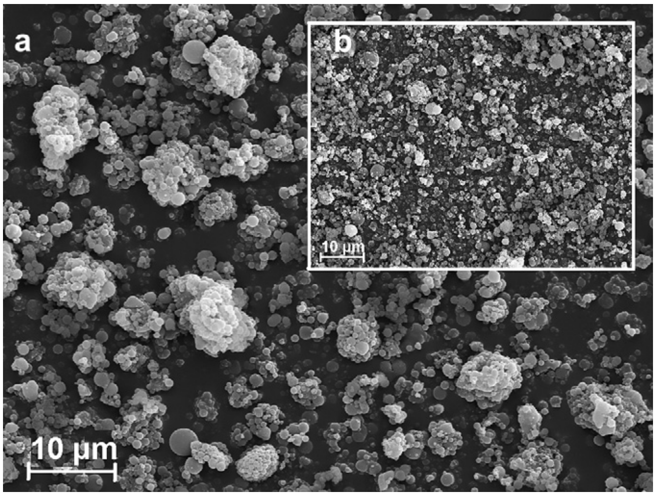


Fig. 2. SEM microphotographs of the pigments obtained after adsorption of C.I. Mordant Red 11 in concentration of 100 mg/dm^3 on (a) unmodified and (b) aminosilane-modified supports.

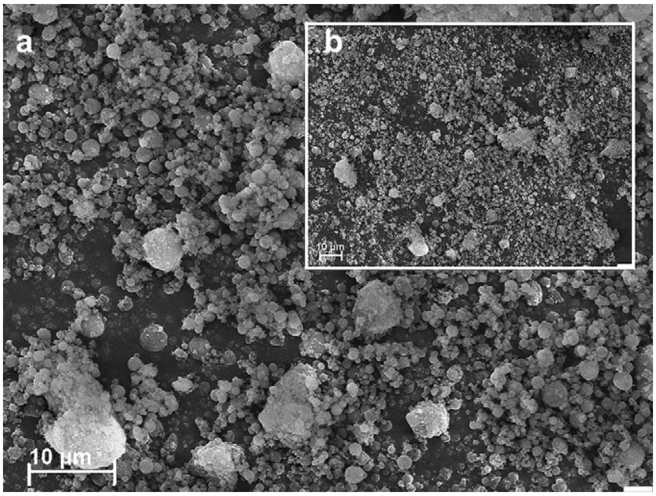
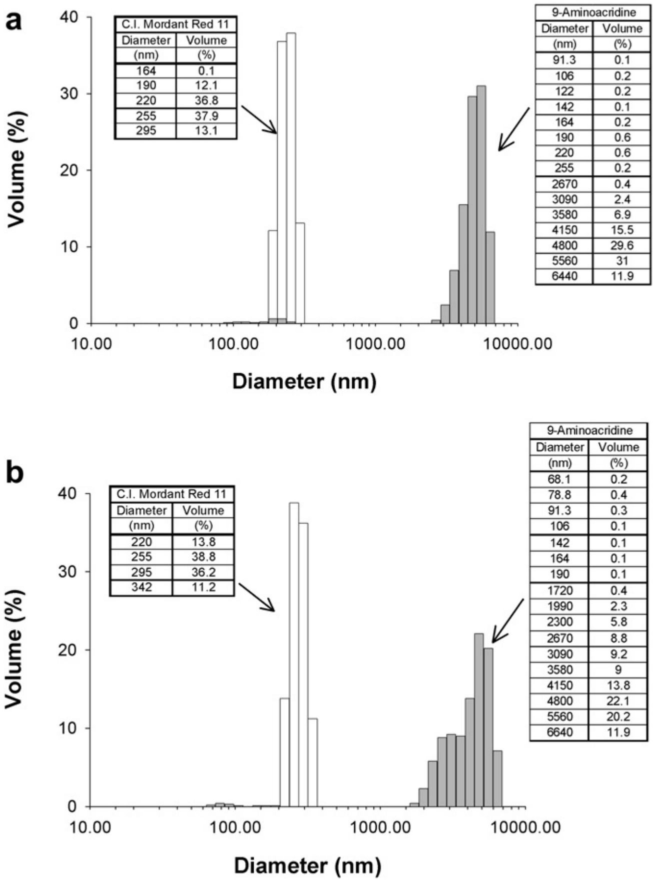


Fig. 3. SEM microphotographs of the pigments obtained after adsorption of 9-AH in concentration of 100 mg/dm^3 on (a) unmodified and (b) aminosilane-modified SiO_2.

The shape and size of the pigment particles influence the rheological properties of the paint, its hue, resistance to atmospheric factors and ease of dispersion. The diameter of the pigment particles usually varies from 1 to 10 μm. If pigment of different



a

C.I. Mordant Red 11	
Diameter (nm)	Volume (%)
164	0.1
190	12.1
220	36.8
255	37.9
295	13.1

9-Aminoacridine	
Diameter (nm)	Volume (%)
91.3	0.1
106	0.2
122	0.2
142	0.1
164	0.2
190	0.6
220	0.6
255	0.2
2670	0.4
3090	2.4
3580	6.9
4150	15.5
4800	29.6
5560	31
6440	11.9

b

C.I. Mordant Red 11	
Diameter (nm)	Volume (%)
220	13.8
255	38.8
295	36.2
342	11.2

9-Aminoacridine	
Diameter (nm)	Volume (%)
68.1	0.2
78.8	0.4
91.3	0.3
106	0.1
142	0.1
164	0.1
190	0.1
1720	0.4
1990	2.3
2300	5.8
2670	8.8
3090	9.2
3580	9
4150	13.8
4800	22.1
5560	20.2
6640	11.9

Fig. 4. Particle size distributions according to volume contribution for the pigments obtained after adsorption of C.I. Mordant Red 11 or 9-aminoacridine used in concentration of 3000 mg/dm^3 on (a) unmodified support and (b) aminosilane-modified SiO_2.

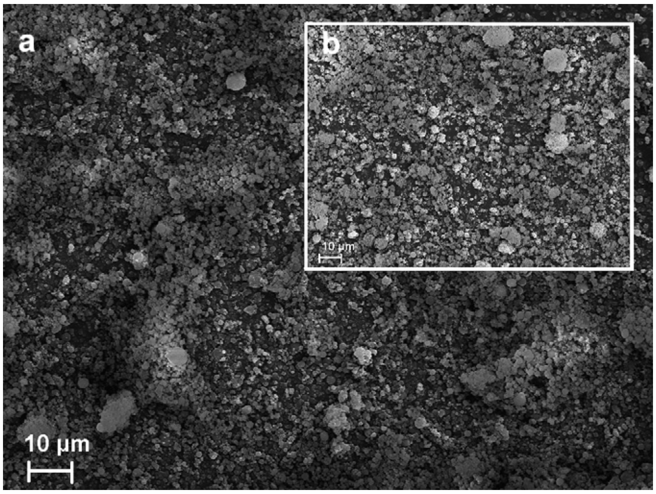


Fig. 5. SEM microphotographs of the pigment composites obtained after adsorption of 9-AH in concentration of 3000 mg/dm^3 on (a) unmodified and (b) aminosilane-modified supports.

particle sizes is added to the paint, then the paint coating will be more resistant to atmospheric factors. The dispersive and morphological properties of pigment composites are of crucial importance for their proper use to get target products of specific properties. Physico-chemical analyses of pigments have been often reported in literature [26,27]. The use of silica precipitated from the emulsion systems as adsorbents of dyes permitted getting pigments of particles of more spherical shape and diameters varying in a smaller range than those of the commercial pigments.

Fig. 1a presents the particle size distributions of the pigments obtained by adsorption of 9-aminoacridine or C.I. Mordant Red 11, in the concentration of 100 mg/dm^3, on the unmodified silica support. The pigment obtained as a result of adsorption of C.I. Mordant Red 11 is more monodisperse; its particle size varies in the range 142 ÷ 220 nm, which is much smaller in comparison with the bimodal distribution evaluated for the pigment obtained using 9-aminoacridine, 142 ÷ 220 nm and 295 ÷ 955 nm.

Modification of the silica support resulted in a considerable increase in the size of pigment particles obtained after adsorption of the dyes, Fig. 1b. The particles of pigment obtained after adsorption of 9-AH show a distinct tendency towards formation of secondary agglomerates. Two bands were obtained in the particle size distribution diagram; the first covered the particle diameter range 79 ÷ 190 nm and the second one – 1990 ÷ 6440 nm. The particles of the diameters from the second band brought much greater volume contribution. As illustrated by the SEM photographs, the pigments obtained as a result of C.I. Mordant Red 11 adsorption (on both unmodified and modified silica) are more monodisperse (Fig. 2a, b) than those obtained using 9-AH (Fig. 3a, b).

A similar tendency was noted for the pigments obtained after adsorption of 9-AH and C.I. Mordant Red 11 in concentration of 3000 mg/dm^3 (Fig. 4). The pigment obtained after adsorption of C.I. Mordant Red 11 is monodisperse and modification of the support had no significant influence on the size of its particles (164 ÷ 295 nm, Figs. 4a and 220 ÷ 342 nm, Fig. 4b). Particles of the pigment obtained after adsorption of 9-AH in concentration of 3000 mg/dm^3 on the unmodified support (compare Figs. 1a and 4a)

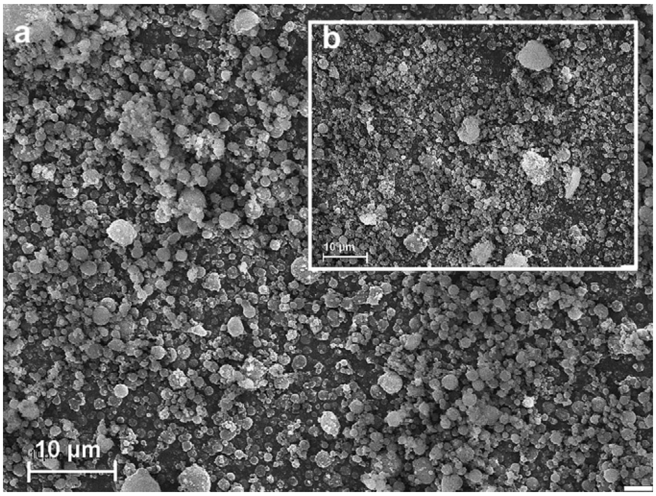


Fig. 6. SEM microphotographs of the pigment composites obtained after adsorption of C.I. Mordant Red 11 in concentration of 3000 mg/dm^3 on (a) unmodified and (b) aminosilane-functionalised supports.

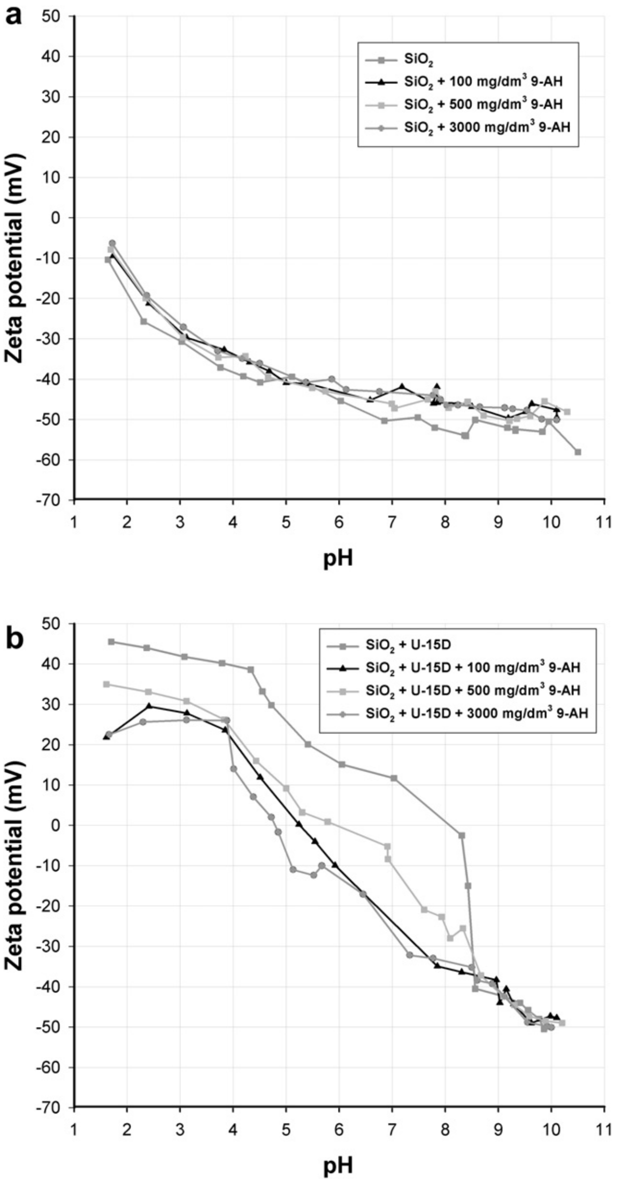


Fig. 7. Zeta potential versus pH for the pigments obtained by adsorption of 9-AH on (a) unmodified and (b) modified silicas.

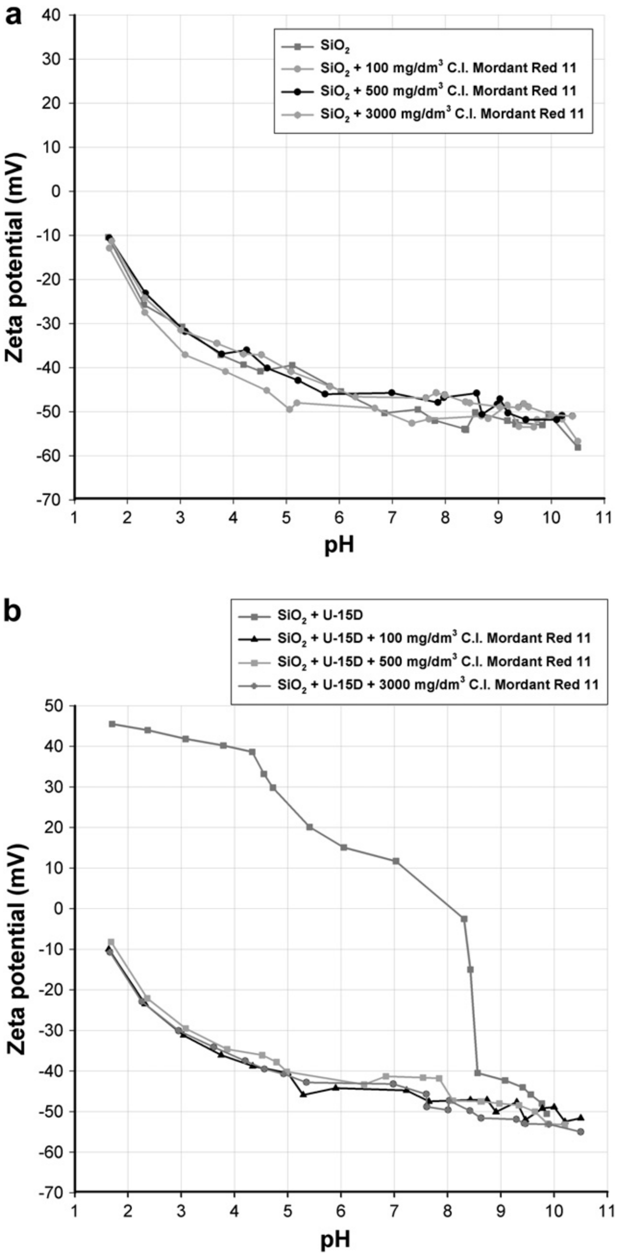


Fig. 8. Zeta potential versus pH for the pigments obtained by adsorption of C.I. Mordant Red 11 on (a) unmodified and (b) modified silicas.

Table 3
Efficiency of adsorption (*W*) and degree of dye elution (*X*) for 9-aminoacridine and C.I. Mordant Red 11 adsorbed on unmodified and modified silicas.

Initial dye concentration (mg/dm^3)	9-Aminoacridine				C.I. Mordant Red 11			
	Unmodified silica		Modified silica		Unmodified silica		Modified silica	
	W (%)	*X* (%)	*W* (%)	*X* (%)	*W* (%)	*X* (%)	*W* (%)	*X* (%)
20	60.4	21.1	62.9	16.8	73.8	23.9	78.6	36.8
40	82.1	12.9	86.5	11.5	74.8	55.3	83.7	38.6
60	85.1	16.8	90.3	14.9	74.9	49.4	86.0	23.3
80	85.8	35.5	88.5	26.7	75.6	28.5	87.2	13.9
100	86.1	27.5	88.9	17.8	76.7	22.5	80.3	8.8
500	86.8	4.9	90.6	3.2	95.5	4.2	86.1	8.3
1000	86.9	5.6	90.8	2.6	67.1	3.7	86.6	6.2
1500	87.8	2.5	88.2	1.6	77.3	11.3	87.2	4.7
2000	88.1	2.4	88.9	1.3	86.2	13.4	90.1	4.1
3000	88.6	5.5	89.6	0.6	88.8	12.8	91.4	3.4

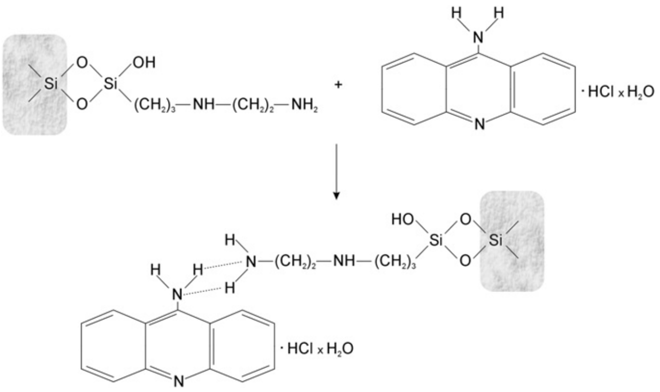


Fig. 9. Mechanism of hydrogen bond formation between 9-AH molecule and the aminosilane-functionalised silica surface.

form larger agglomerate structures. The dominant volume contribution comes from the particles of diameters from the ranges 91 ÷ 255 nm and 2670 ÷ 6440 nm, so from those corresponding to agglomerates. Modification of the support, similarly as for C.I. Mordant Red 11, had no significant influence on the size of the pigment particles; the dominant volume contribution was brought by the particles of diameters from the ranges: 68 ÷ 106 nm, 142 ÷ 190 nm and 1720 ÷ 6640 nm.

As follows from SEM images (Figs. 5 and 6) showing the morphology of the samples, the particles of the hybrid systems SiO_2 + C.I. Mordant Red 11 are spherical in shape. The pigments were highly homogeneous.

Fig. 7 presents the zeta potential versus pH for selected pigment composites obtained as a result of adsorption of 9-AH on unmodified and modified silica support. For the samples studied (Fig. 7a) no isoelectric point was reached (there was no pH value at which zeta potential was 0). For the pigments obtained by adsorption of 9-AH on unmodified silica support negative zeta potential values (−10 ÷ −60 mV) were obtained in the pH range 2 ÷ 11. The electrokinetic curves obtained for the pigments made of 9-AH adsorbed on the modified silica (Fig. 7b) differ significantly from those

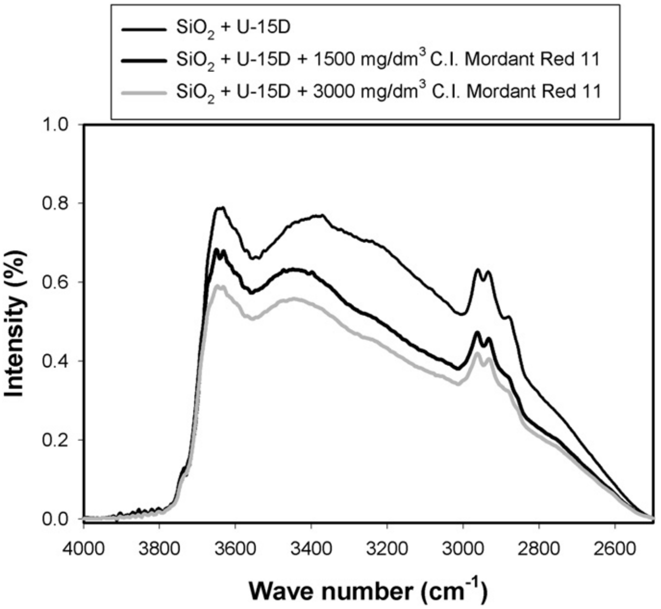


Fig. 10. FT-IR spectrum of the modified silica and pigments obtained by adsorption of C.I. Mordant Red 11.

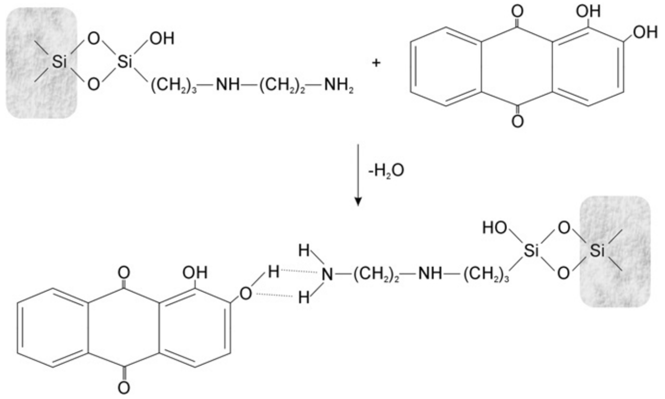


Fig. 11. Mechanism of hydrogen bond formation between C.I. Mordant Red 11 and the aminosilane-modified silica surface.

recorded for the same dye adsorbed on the unmodified silica. The electrokinetic curve of SiO_2 modified with 3 wt./wt. of U-15D silane, shows the isoelectric point IEP at 8.35. For the pigment composites obtained on this support the isoelectric points fall in the range 4.22 ÷ 6.09. Such a significant shift of the isoelectric point towards higher pH values is explained by a strong protonation effect of the amine groups coming from aminosilane (the modifier) and the amine group from 9-AH. Dissociation of these groups is an important factor leading to changes in the surface charge of the pigments. When the density of H^+ ions is high, the $-NH_3^+$ groups are induced and positive charge appears on the modified silica surface. With further increase in the density of H^+ ions the process of dissociation is restricted and the surface charge of the pigments decreases. The zeta potential of the pigments obtained on the modified silica is positive almost in the whole acidic pH range. The above electrokinetic behaviour can be described by the exemplary equations (1)–(2):

$$-NH_2 + H^+ \rightarrow -NH_3^+ \tag{1}$$

$$-NH_2 + OH^- \rightarrow -NH^- + H_2O \tag{2}$$

For the pigment based on C.I. Mordant Red 11 adsorbed on the unmodified or modified support, no significant changes were noted in the electrokinetic curves (Fig. 8a, b). The character of these electrokinetic curves did not change even on increasing concentration of the C.I. Mordant Red 11 solution. Almost in the whole pH range the zeta potential assumed negative values.

Table 3 gives the efficiency of adsorption of 9-AH and C.I. Mordant Red 11 on the unmodified or modified silica support and the pigments stability (degree of dye elution). The efficiency of 9-AH adsorption on the unmodified silica varies in the range 40.4 ÷ 88.6%, while on the modified support it significantly increases (the most pronounced increase is noted for the initial solution of the lowest concentration of 20 mg/dm^3).

The low degree of 9-AH elution from the modified silica support indicates the higher stability and chemical affinity of the dye bonding with the silica surface, which is important from the point of view of pigments application as it informs on the pigment's behaviour when exposed to water. Similarly as for C.I. Mordant Red 11, the degree of 9-AH elution decreases with increasing concentration of the dye in the solution used for the pigments preparation. Relatively small efficiency of 9-AH adsorption on the unmodified silica suggest that no chemical reaction takes place between the dye and the silica surface. Modification of silica leads to a decrease in the dye elution from the support, which suggests the stronger interactions between the dye and silane on the silica support. The efficiency of 9-AH adsorption significantly increases on the silica modified with silane. Most probably, on the surface of the support modified with aminosilane the hydrogen bonds are formed between the amine groups of the aminosilane and the dye molecule, see Fig. 9. Modification of the support surface with aminosilane changes its hydrophilic/hydrophobic character and increases the affinity of the functionalised silica support to the dye.

The mechanism of adsorption proposed is confirmed by the data on the dye elution given in Table 3. Desorption of C.I. Mordant Red 11 and 9-AH from silica surface suggests the physical nature of adsorption and formation of weak hydrogen bonds.

The efficiency of C.I. Mordant Red 11 adsorption on the unmodified support (Table 3) is comparable to that of 9-AH. Modification of the support surface has increased a little the efficiency of C.I. Mordant Red 11 adsorption. The degree of C.I. Mordant Red 11 elution from the unmodified silica support is rather large for the pigment composites obtained from the dye solutions of low concentrations of 40, 60 and 80 mg/dm^3 for which it reaches 55.3%, 49.4% and 28.5%, respectively. For the higher dye concentrations in the solutions used, the degree of elution is smaller and varies from 3.7% to 23.9%.

Confirmation of the chemical character of the modification is brought by the FT-IR spectrum (Fig. 10). The FT-IR spectrum of the modified silica and pigment composites obtained by adsorption of C.I. Mordant Red 11 show the band at 3660 cm^{-1} assigned to the silanol groups present on the silica surface. For the C.I. Mordant Red 11 adsorbed on modified silica support the intensity of this band decreases with increasing concentration of C.I. Mordant Red 11 in the solution used to make the pigment composites. The spectrum also shows the band assigned to the stretching C—H vibrations in the range 2965 ÷ 2850 cm^{-1} and the band corresponding to the physically bound water, in the range 3600 ÷ 3200 cm^{-1}. The most

Table 4
Colorimetric data for the pigments obtained by adsorption of 9-aminoacridine from solutions of different concentration on the unmodified and modified silicas.

Initial dye concentration (mg/dm^3)	Unmodified silica						Modified silica					
	*L**	*a**	*b**	*c**	*h**	Δ*E**	*L**	*a**	*b**	*c**	*h**	Δ*E**
0	94.62	−0.07	3.13	3.13	86.85	–	92.91	−3.19	14.59	15.03	92.34	–
20	93.98	−0.48	3.00	2.90	90.48	0.84	93.52	0.12	2.91	2.91	99.59	0.82
40	93.28	−0.62	3.20	3.26	92.22	3.01	92.92	−0.12	3.09	3.09	100.96	0.53
60	90.05	−0.93	2.45	2.62	107.58	1.05	92.32	−0.89	2.80	2.94	110.82	4.08
80	89.95	−1.14	2.93	3.15	104.64	1.55	91.25	−0.80	3.07	3.17	111.21	4.18
100	87.34	−1.63	2.66	3.12	112.61	1.87	90.56	−1.30	3.12	3.38	121.56	6.85
500	86.97	−2.39	4.91	5.46	117.46	3.88	89.91	−2.88	5.54	6.24	115.96	7.64
1000	86.75	−4.54	9.07	10.14	115.99	9.03	89.53	−4.93	10.10	11.24	116.6	8.63
1500	86.16	−5.81	11.73	13.09	115.69	7.98	88.88	−4.56	9.48	10.52	116.34	12.46
2000	85.77	−6.43	14.26	15.65	112.52	12.52	88.63	−5.81	14.01	15.16	114.28	13.93
3000	85.66	−7.63	18.29	19.81	110.41	15.75	87.83	−6.16	16.55	17.66	112.64	17.57

Table 5
Colorimetric data for the pigment composites obtained by adsorption of C.I. Mordant Red 11 from solutions of different concentration on the unmodified and modified silicas.

Initial dye concentration (mg/dm^3)	Unmodified silica						Modified silica					
	L^*	a^*	b^*	c^*	h^*	ΔE^*	L^*	a^*	b^*	c^*	h^*	ΔE^*
0	94.62	−0.07	3.13	3.13	86.85	–	92.91	−3.19	14.59	15.03	92.34	–
20	89.68	4.92	3.06	5.79	31.87	6.5	88.8	3.89	2.75	4.76	35.29	5.62
40	88.05	5.83	2.92	6.5	26.41	8.26	87.64	4.38	2.72	5.16	31.8	6.08
60	86.98	6.28	2.89	6.93	24.95	9.35	85.95	5.09	2.86	5.84	29.33	7.07
80	85.54	5.82	2.28	6.25	21.41	10.19	84.73	4.81	2.42	5.38	26.76	7.04
100	84.38	5.67	1.91	5.98	18.6	11.1	83.61	4.96	2.44	5.52	26.23	7.23
500	81.39	8.49	1.31	8.59	8.78	15.19	80.94	6.43	0.46	6.45	4.07	12.92
1000	77.49	9.06	−0.66	9.09	355.81	19.05	75.63	8.00	−1.98	8.24	346.08	19.64
1500	63.39	8.61	−3.49	9.29	337.97	32.29	60.74	6.61	−4.63	8.07	325.02	34.65
2000	49.48	9.94	−5.02	11.13	333.21	46.15	45.24	7.74	−6.11	9.86	321.74	45.84
3000	49.36	7.44	−3.92	8.41	−3.92	8.41	42.84	7.53	−5.61	9.39	−5.61	9.39

probable mechanism of C.I. Mordant Red 11 adsorption of the physical character can be proposed (Fig. 11).

Table 4 presents results of colorimetric analysis performed in the CIE $L^*a^*b^*$ system for the pigments of 9-AH adsorbed on unmodified or modified silica support. The pigment composites obtained by adsorption of 9-AH on unmodified SiO_2 were yellow. With increasing concentration of the dye in the solution used for pigments preparation the lightness of the pigments (L^*) decreased. In the cases of the pigments obtained using modified silica the same tendency was observed, as L^* decreased from 92.91 to 87.83 (Table 4).

With increasing concentration of 9-AH in the initial solution, the samples became greener/yellower, this increase being greater for the dyes supported on the modified silica. Table 5 shows the colorimetric data for the pigments obtained by adsorption of C.I. Mordant Red 11 on the unmodified and modified silica supports. With increasing concentration of C.I. Mordant Red 11 in the initial solution, irrespective of the support type, the samples became bluer (i.e., increased negative b^* values).

With increasing concentration of C.I. Mordant Red 11 in the initial solution, the lightness of the pigments obtained using the modified silica as support decreased. Moreover, the L^* value of the pigments prepared applying the unmodified silica support was greater that of the C.I. Mordant Red 11 adsorbed on the modified silica, for the same concentrations of the dye in the initial solution. The chroma of the samples prepared using the modified silica was higher than the pigment obtained on the unmodified SiO_2. Table 6 shows the calculated degree of silica coverage obtained for 9-AH and C.I. Mordant Red 11 for different concentrations of the dye solutions used for the pigment composites preparation.

The degree of coverage of the modified silica support with the dye evaluated on the basis of the Berendsen and de Golan equation [28] increases from 2.848 to 3.141 μmol/m^2 with increasing concentration of 9-AH in the initial solution – see Table 6. It is greater for the modified than for unmodified silica; the degree of coverage of the unmodified silica with 9-AH from the solution of 20 mg/dm^3 was 1.747 μmol/m^2, while that of the modified silica with 9-AH from the same solution was as much as 2.848 μmol/m^2. The degree of coverage of the unmodified silica with C.I. Mordant Red 11 increases with increasing concentration of this dye in the initial solution. For the dye concentrations from the range 20 ÷ 1000 mg/dm^3 the degree of coverage is low, from 0.932 μmol/m^2 at 20 mg/dm^3 to 1.067 μmol/m^2 at 1000 mg/dm^3, while for higher dye concentrations the degree of coverage significantly increases, up to 4.29 μmol/m^2 at 3000 mg/dm^3. The highest degree of coverage (4.904 μmol/m^2) of the modified silica with C.I. Mordant Red 11 was reached for the highest dye concentration in the initial solution (3000 mg/dm^3).

The hydrophilic/hydrophobic character of the pigments obtained was evaluated on the basis of the wettability (with water) and sedimentation profiles (Figs. 12 and 13). Sedimentation tests confirmed that the pigments obtained after adsorption of C.I. Mordant Red 11 or 9-aminoacridine onto unmodified silica support are more hydrophilic and that is why their sedimentation was faster (especially of the

Table 6
The degree of coverage of the unmodified and modified silicas with 9-aminoacridine and C.I. Mordant Red 11 adsorbed from solutions of different concentration.

Initial dye concentration (mg/dm^3)	9-Aminoacridine		C.I. Mordant Red 11	
	Unmodified silica	Modified silica	Unmodified silica	Modified silica
20	1.747	2.848	0.932	1.830
40	1.749	2.853	0.935	1.832
60	1.757	2.860	0.938	1.834
80	1.759	2.860	0.952	1.839
100	1.761	2.860	0.960	1.850
500	1.878	2.942	1.013	1.942
1000	1.915	3.049	1.067	2.093
1500	2.138	3.082	2.674	3.468
2000	2.311	3.116	3.641	4.640
3000	2.901	3.141	4.290	4.904

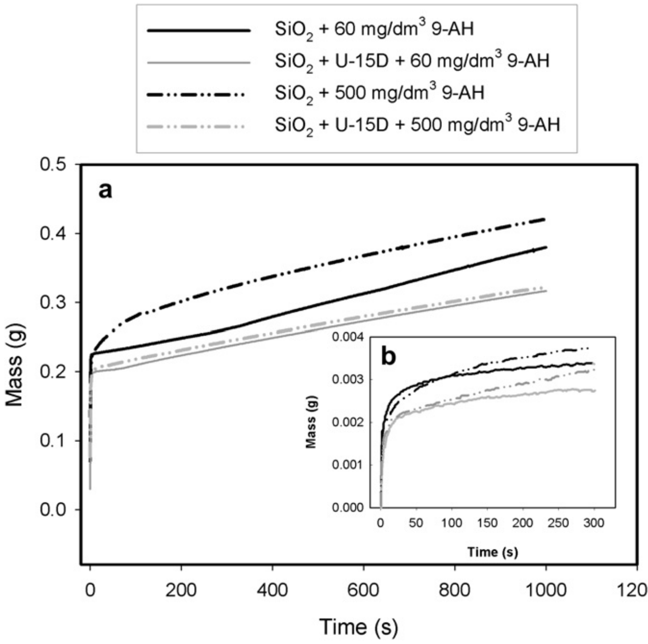


Fig. 12. Profiles of (a) wettability and (b) sedimentation in water for the selected pigment composites obtained after adsorption of 9-aminoacridine on the surface of SiO_2.

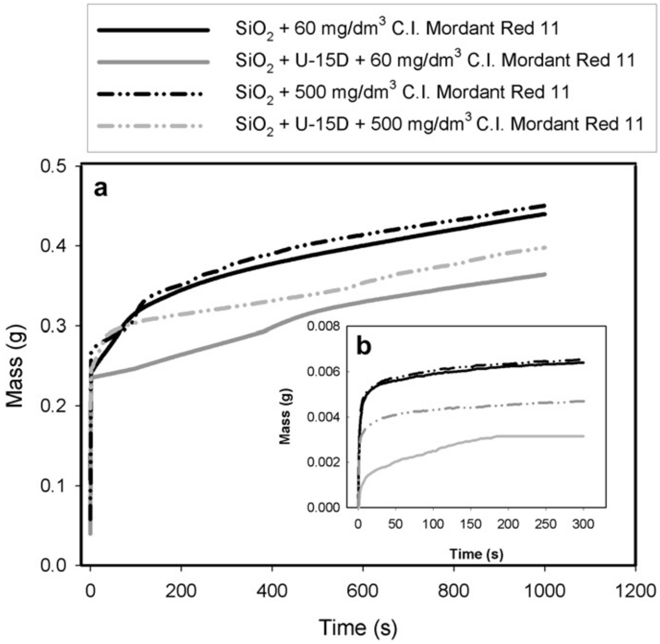


Fig. 13. Profiles of (a) wettability and (b) sedimentation in water for the pigment composites obtained after adsorption of C.I. Mordant Red 11 on unmodified and modified SiO_2 supports.

samples: SiO_2 + 60 mg/dm^3 of 9-AH, SiO_2 + 500 mg/dm^3 of 9-AH, SiO_2 + 60 mg/dm^3 of C.I. Mordant Red 11, and SiO_2 + 500 mg/dm^3 of C.I. Mordant Red 11). The pigments obtained applying modified silica support were more hydrophobic and their sedimentation was much slower.

4. Conclusions

The above presented and discussed results have proved that preliminary modification of silica support improves the efficiency of adsorption of organic dyes. The modification enhances the chemical affinity of the silica surface to the functional groups of the organic dyes. Functionalisation of the silica surface with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane has brought about an increased tendency to agglomeration of particles (the band assigned to agglomerates structures is moved from 1110 ÷ 3090 nm to 1720 ÷ 6440 nm), and changed the electrokinetic properties of the pigment composites. For the unmodified silica the zeta potential values were negative in the whole pH range, whereas after modification with aminosilane the electrokinetic curves and the isoelectric point were shifted towards higher pH values. For the silica modified with aminosilane the zeta potential values were positive in a wide pH range.

The degree of dye elution from the silica surface was found rather low for the majority of samples, which proves that the pigment composites were obtained as a result of high sorption affinity of the dye to the aminosilane-modified silica support. Modification of silica was also found to reduce the degree of dye elution from the SiO_2 support. The degree of elution was smaller for 9-aminoacridine, which has basic character, than for C.I. Mordant Red 11.

Results of the colorimetric analysis have shown that with increasing concentration of the dye solutions used for making pigments the brightness of the pigments decreases. Moreover, as follows from the results, by changing the dye concentration in the initial solution it is possible to regulate the hue of the pigment composites obtained on the silica supports.

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References

[1] Yuan J, Xing W, Gu G, Wu L. The properties of organic pigment encapsulated with nano-silica via layer-by-layer assembly technique. Dyes Pigm 2008;76:463–9.
[2] Lelu S, Novat C, Graillat C, Guyot A, Bourgeat-Lami E. Encapsulation of an organic phthalocyanine blue pigment into polystyrene latex particles using a miniemulsion polymerization process. Polym Int 2003;52:542–7.
[3] Zhang T, Fei X, Wang S, Zhou Ch. Pigmentation of Vat Blue RS by ball milling in solvents. Dyes Pigm 2000;45:15–21.
[4] Krysztafkiewicz A, Jesionowski T. Układy hybrydowe krzemionka-barwnik organiczny: otrzymywanie i zastosowanie. Przem Chem 2003;82:844–6.
[5] Bugnon P. Surface treatment of pigments. Treatment with inorganic materials. Prog Org Coat 1996;29:39–43.
[6] Yuan JJ, Zhou SX, Wu LM, You B. Organic pigment particles coated with titania via sol–gel process. J Phys Chem B 2006;110:388–94.
[7] Hosseini-Zori M, Taheri-Nassaj E, Mithabibi AR. Effective factors on synthesis of the hematite-silica red inclusion pigment. Ceram Int 2008;34:491–6.
[8] Bondioli F, Manfredini T, Siligardi C, Ferrari AM. New glass–ceramic inclusion pigment. J Am Ceram Soc 2005;88:1070–4.
[9] Garcia A, Llusar M, Badenes J, Tena MA, Monros G. Encapsulation of hematite in zircon by microemulsion and sol–gel methods. J Sol-Gel Sci Technol 2003;27:267–75.
[10] Doskocz M, Kubas K, Frąckowiak A, Gancarz R. NMR ab initio studies of Mg^{2+}, Ca^{2+}, Zn^{2+}, Cu^{2+} alizarin complexes. Polyhedron 2009;28:2201–5.
[11] Angelini LG, Pistelli L, Belloni P, Bertoli A, Panconesi S. *Rubia tinctorum* a source of natural dyes: agronomic evaluation, quantitative analysis of alizarin and industrial assays. Ind Crop Prod 1997;6:303–11.
[12] Campos-Martin JM, Blanco-Brieva G, Fierro JLG. Hydrogen peroxide synthesis: an outlook beyond the anthraquinone process. Angew Chem Int Ed 2006;49:6962–84.
[13] Vasconsuleo A, Boland R. Molecular aspects of the early stages of elicitation of secondary metabolites in plants. Plant Sci 2007;172:861–75.
[14] Cañamares MV, García-Ramos JV, Domingo C, Sánchez-Cortes S. Surface enhanced Raman scattering study of the adsorption of the anthraquinone pigment alizarin on Ag nanoparticles. J Raman Spectrosc 2004;35:921–7.
[15] Epstein M, Yariv S. Visible-specroscopy study of the adsorption of alizarine by Al-montmorillonite in aqueous suspensions and in solid state. J Colloid Interface Sci 2003;263:377–85.
[16] Wu Z, Joo H, Ahn IS, Haam S, Kim JH, Lee K. Organic dye adsorption on mesoporous hybrid gels. Chem Eng J 2004;102:277–82.
[17] Harris RG, Wells JD, Johnson BB. Selective adsorption of dyes and other organic molecules to kaolinite and oxide surfaces. Colloids Surf A 2001;180:131–40.
[18] Miliani C, Romani A, Favaro G. Acidichromic effects in 1,2-di- and 1,2,4-trihydroxyanthraquinones. A spectrophotometric and colourimetric study. J Phys Org Chem 2000;13:141–50.
[19] Scheweppe H, Winter J. Artists' pigments. In: FitzHugh EW, editor. A Handbook of their History and characteristics, vol. 3. Oxford: Oxford University Press; 1998. p. 109.
[20] Takahashi E, Fujita K, Kamataki T, Arimoto-Kobayashi S, Okamoto K, Negishi T. Inhibition of human cytochrome P450 1B1, 1A1 and 1A2 by antigenotoxic compounds, purpurin and alizarin. Mutat Res 2002;508:147–56.
[21] Murza A, Sanchez-Cortes S, Garcia-Ramos JV, Guisan JM, Alfonso C, Rivas G. Interaction of the antitumor drug 9-aminoacridine with guanidinobenzoatase studied by spectroscopic methods: a possible tumor marker probe based on the fluorescence exciplex emission. Biochemistry 2000;39:10557–65.
[22] Loechler EL, King J. Identification of the 9-aminoacridine/DNA complex responsible for photodynamic inactivation of P22t. Biochemistry 1986;25:5858–64.
[23] Steven FS, Griffin MM, Blakey DC, Talbot IC, Hanski C, Bell J. Further evidence for different isoenzymic forms of a cell surface protease, quanidinobenzoatase, associated with tumours. Anticancer Res 1992;12:2159–64.
[24] Jesionowski T, Krysztafkiewicz A. Comparison of the techniques used to modify amorphous hydrated silicas. J Non-Cryst Solids 2000;277:45–57.
[25] Jesionowski T, Binkowski S, Krysztafkiewicz A. Adsorption of the selected organic dyes on the functionalized surface of precipitated silica via emulsion route. Dyes Pigm 2005;65:267–79.
[26] Binkowski S, Jesionowski T, Krysztafkiewicz A. Preparation of pigments on modified precipitated silica. Dyes Pigm 2000;47:247–57.
[27] Andrzejewska A, Krysztafkiewicz A, Jesionowski T. Treatment of textile dye wastewater using modified silica. Dyes Pigm 2007;75:116–24.
[28] Berendsen GE, de Golan L. Preparation and chromatographic properties of some chemically bonded phases for reversed–phase liquid chromatography. J Liq Chrom Relat Tech 1978;1:561–86.