

Treatment of textile dye wastewater using modified silica

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Received 5 April 2006; received in revised form 22 May 2006; accepted 22 May 2006

Available online 18 July 2006

Abstract

In this work a 'carrier' was selected that would separate an anionic reactive dye from aqueous solution, and would display an intense white colour and a high adsorptive capacity. In this context, a commercial, highly dispersed precipitate, Syloid[®] 244 silica was employed to remove C.I. Reactive Blue 19. The adsorption resulted in blue pigmentation of the silica carrier; the ensuing pigment was subjected to a comprehensive physicochemical analysis, including particle size, particle size distribution, polydispersity, tendency to form primary and secondary agglomerates and the morphology of the particle surface. It was found that a preliminary surface modification of the silica adsorbent with an NH₂-silane compound was necessary. The aminosilane-modified silica could be used as a selective adsorbent in the purification of waste dye solutions; its application secured highly efficient removal of dye from solutions (in most cases over 90% and in some cases even 100%). The silica-carrier product was then used as a pigment within an exterior acrylic paint. Optimum properties were obtained using 5% silane; the ensuing pigment displayed very low polydispersity (0.030), low mean particle diameter (428 nm) and no tendency to form secondary agglomerates.

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Keywords: Precipitated silica; Surface modification; 3-Aminopropyltriethoxysilane; Adsorption of organic dye

1. Introduction

The increasing amounts of sewage and industrial sewage in particular pose serious threats to natural environment. Industrial sewage results from technological processes in several branches of industry, i.e., in mining, metallurgy, plants producing paints and varnishes, in textile, chemical and petrochemical industries. Various techniques for removing dyes from wastes have been developed, including extraction [1], membrane processes [2] and destructive oxidation [3]. Adsorptive processes are of high significance [4] and industrial adsorbents include activated carbon, active Al₂O₃, zeolites or gels of silicic acid [5–8].

Silica particles manifest a hydrophilic surface due to the presence of silanol groups. The groups are weakly acidic

and are very reactive; moreover, they allow chemical modification of the silica surface. Modification of silica exerts a pronounced effect on the chemical nature and properties of its surface. Pro-adhesive compounds adsorbed on silica surface induce hydrophobic transformation of the surface and provide it with an organophilic form [9–12].

The adsorption of a dye on a silica surface involves first its modification with, e.g., aminosilane coupling agent, in order to bind the silane chain to the surface; next, a dye solution reacts with the silica surface-coupled silane [13,14]. In this way a pigment can be obtained which contains the dye, stably bound by covalent bonds or hydrogen bonds. The dye, thus coupled cannot be desorbed with solvents [15].

The suggested approach allows purification of textile dyeing wastes. In parallel, new products are obtained namely pigments of interesting colour and good physicochemical parameters. Supplementation with modifiers opens potential for control of dye adsorption processes on the silica surface and products of optimum parameters.

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Table 1
Physicochemical properties of the silica before and after modification with aminosilane

Symbol of sample	Solvent	Amount of silane (w/w)	Bulk density (g dm ⁻³)	Water absorbing capacity (cm ³ × 100 g ⁻¹)	Dibutyl phthalate absorbing capacity (cm ³ × 100 g ⁻¹)	Paraffin oil absorbing capacity (cm ³ × 100 g ⁻¹)
0	—	—	59.3	850	1400	1900
I-3	Toluene	3	77.3	600	1300	1450
I-5		5	90.8	650	1200	1800
II-3	Acetone	3	88.3	600	1400	1500
II-5		5	84.6	650	1300	1800
III-3	Methanol/water	3	84.4	600	1300	1650
III-5		5	82.7	550	1200	1500
IV-3	Methanol	3	88.6	600	1400	1550
IV-5		5	78.3	650	1400	1700
V-3	Water	3	86.6	500	1300	1500
V-5		5	83.6	550	1300	1600

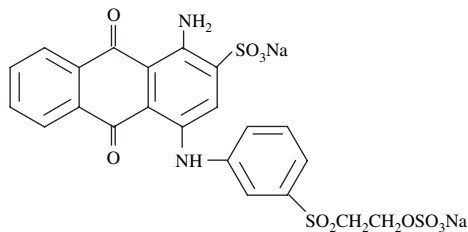
2. Experimental

2.1. Materials

Precipitated Syloid[®] 244 silica (Grace Davison) was used. Silica surface modification was performed using a silane coupling agent, 3-aminopropyltriethoxysilane (U-13), H₂N(CH₂)₃Si(OC₂H₅)₃ produced by UniSil.

Water, methanol, methanol/water solution (4:1), acetone or toluene were used as silane solvents.

The textile wastes contained C.I. Reactive Blue 19 of the following formula:



2.2. Procedures and methods

2.2.1. Modification of the silica surface

The surface of Syloid[®] 244 silica was modified using 3-aminopropyltriethoxysilane (U-13). Solutions containing 3 or 5 parts by mass of the modifier were prepared in appropriate solvents, calculated per 100 parts by mass of the SiO₂. The volume of the modifier solution was selected so as to assure uniform wetting of the silica surface. The modification was performed in a mixer [16], for 1 h. Solvents were separated by distillation.

2.2.2. Preparation of an organic dye containing-waste solution

Dye concentrations of 25, 50 or 300 mg of the dye per 1 dm³ solution were employed. A defined volume (50 cm³) of the waste dye solution was introduced to a reactor, in which the purification was performed by adsorptive technique.

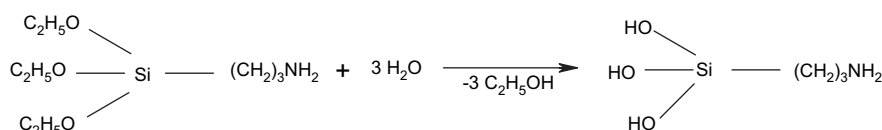
2.2.3. Purification procedure

A reactor, containing the textile waste of known dye concentration, was charged with various (1, 2, 3, 4 g) amounts of silica. The content was mixed for 30 min at room temperature and the resulting solution was filtered off under vacuum. The obtained pigment was dried by convection and the filtrate was then analysed for the amount of dye remaining by measuring the absorbance of the dye solution using a Spekol 1200 spectrophotometer at λ_{max} = 594 nm to establish the extent of dye removal from the waste solution following adsorption on the silica.

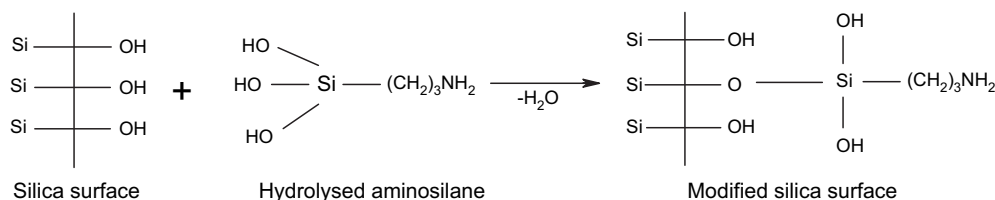
The potential to desorb the dye from pigment surface was also tested. For this purpose an aqueous suspension of the pigment was mixed for 1 h at room temperature. In the filtrate, concentration of soluble pigment components was estimated by the absorbance measurements.

2.2.4. Physicochemical properties of the examined silicas

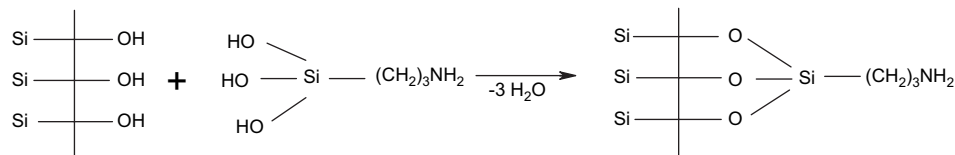
Principal physicochemical tests on unmodified and modified silicas were conducted as described earlier [17]. Estimated variables included bulk density, capacities to absorb water, dibutyl phthalate and paraffin oil. Size of particles, particle size distribution, polydispersity, tendency to form aggregates and agglomerates were also estimated.



Scheme 1.



Scheme 2.



Scheme 3.

2.2.5. Physicochemical properties of the obtained pigments

Studies of the morphology and microstructure of the pigments were performed to obtain data on the dispersion, particle size, surface morphology and structure of individual particles and on the type of pigment aggregation and agglomeration. The studies were conducted using a Philips SEM 515 microscope; dynamic light scattering (DLS) employing

a ZetaPlus instrument permitted information of the multi-modal particle size distribution pattern to be achieved on the basis of autocorrelative functions of laser light beam (670 nm) scatter. The most important parameters obtained using this technique included polydispersity and an effective particle diameter. The effective particle diameter was estimated according to the following formula:

$$D_{\text{eff}} = \sum Nd^6 / \sum Nd^5$$

where N denotes number of particles and d denotes diameter of examined particles.

Table 2

Extent of removal of C.I. Reactive Blue 19 from waste solution following adsorption on the silica modified with aminosilane

Symbol of sample	Solvents	Amount of added silica (g)	Dye concentration after adsorption (mg dm^{-3})	Extent of dye removal (%)
<i>Unmodified silica</i>				
25 RB 0-0-1	—	1	0.0247	1.2
25 RB 0-0-2	—	2	0.0241	3.6
<i>Modified silica</i>				
3 Parts (w/w) of silane U-13				
25 RB I-3-1	Toluene	1	0.0012	95.2
25 RB I-3-2		2	0.0001	99.6
25 RB II-3-1	Acetone	1	0.0009	96.4
25 RB III-3-1	Methanol/water	1	0.0004	98.4
25 RB III-3-2		2	0.0001	99.6
25 RB IV-3-1	Methanol	1	0.0022	91.2
25 RB IV-3-2		2	0.0009	96.4
25 RB V-3-1	Water	1	0.0005	98.0
25 RB V-3-2		2	0.0002	99.2
5 Parts (w/w) of silane U-13				
25 RB I-5-1	Toluene	1	0.0001	99.6
25 RB I-5-2		2	0	100.0
25 RB I-5-3		3	0	100.0
25 RB II-5-1	Acetone	1	0.0031	87.6
25 RB II-5-2		2	0.0017	93.2
25 RB III-5-1	Methanol/water	1	0.0023	90.8
25 RB III-5-2		2	0	100.0
25 RB IV-5-1	Methanol	1	0.0002	99.2
25 RB IV-5-2		2	0	100.0
25 RB IV-5-4		4	0	100.0
25 RB V-5-1	Water	1	0.0012	95.2
25 RB V-5-2		2	0.0010	96.0

Concentration of dye employed before adsorption is 25 mg dm^{-3} .

Table 3

Extent of removal of C.I. Reactive Blue 19 from waste solution following adsorption on the silica modified with aminosilane

Symbol of sample	Solvents	Amount of added silica (g)	Dye concentration after adsorption (mg dm^{-3})	Extent of dye removal (%)
3 Parts (w/w) of silane U-13				
50 RB I-3-1	Toluene	1	0.0001	99.8
50 RB I-3-2		2	0	100.0
50 RB I-3-3		3	0	100.0
50 RB III-3-1	Methanol/water	1	0.0009	98.2
50 RB III-3-3		3	0.0003	99.4
50 RB IV-3-1	Methanol	1	0.0004	99.2
50 RB IV-3-2		2	0.0001	99.8
50 RB V-3-1	Water	1	0.0010	98.0
50 RB V-3-2		2	0.0006	98.8
50 RB V-3-3		3	0.0005	99.0
5 Parts (w/w) of silane U-13				
50 RB I-5-1	Toluene	1	0	100.0
50 RB I-5-2		2	0	100.0
50 RB I-5-3		3	0	100.0
50 RB III-5-1	Methanol/water	1	0.0008	98.4
50 RB III-5-3		3	0.0006	98.8
50 RB IV-5-1	Methanol	1	0.0008	98.4
50 RB IV-5-2		2	0	100.0
50 RB V-5-1	Water	1	0.0001	99.8
50 RB V-5-2		2	0	100.0
50 RB V-5-3		3	0	100.0

Concentration of dye employed before adsorption is 50 mg dm^{-3} .

Table 4
Extent of removal of C.I. Reactive Blue 19 dye from waste solution following adsorption on the silica modified with 5 parts (w/w) of aminosilane U-13

Symbol of sample	Solvents	Amount of added silica (g)	Dye concentration after adsorption (mg dm^{-3})	Extent of dye removal (%)
300 RB I-5-2	Toluene	2	0.0020	99.3
300 RB I-5-3		3	0.0010	99.7
300 RB IV-5-2	Methanol	2	0.0019	99.4
300 RB IV-5-3		3	0.0014	99.6

Concentration of dye employed before adsorption is 300 mg dm^{-3} .

2.2.6. Application of the pigments in paints

The obtained pigment was used in a solvent acrylic paint for exterior use, *AKRYBET*. The scope of tests included density, viscosity, drying time, quality of coating, resistance to scrubbing as well as adherence to bed. The composition of the paint was as follows: acrylic dispersion 15%, titanium dioxide 16%; carbonate filler (precipitated calcium carbonate) 40%; wetting agents, dispersion-inducing agents and densifiers 1%; organic solvent 28%.

In the paint, TiO_2 was substituted by the pigment obtained from the waste purification (11%).

3. Results and discussion

The physicochemical properties of the silica before and after modification with aminosilane are given in Table 1.

Following the aminosilane modification, the silica displayed higher bulk density (independent of the type of solvent and amounts of the modifier used). An evident hydrophobic transformation of the modified silica surface could be concluded from decreasing capacities to absorb water (even to $500 \text{ cm}^3 \times 100 \text{ g}^{-1}$ for silica modified with 3 weight parts of aminosilane, as compared to $850 \text{ cm}^3 \times 100 \text{ g}^{-1}$ for the unmodified silica).

Modification of the silica surface progressed as follows; at first aminosilane hydrolysis took place (see Scheme 1).

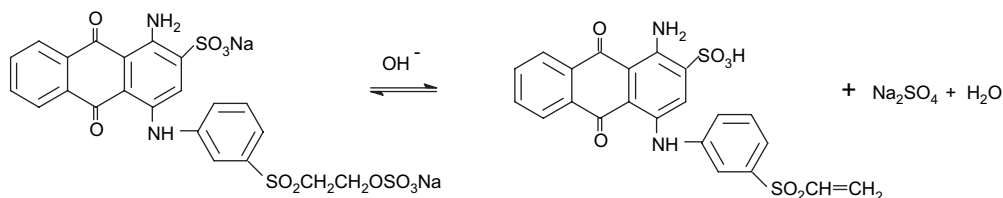
At the lower concentration of silane (e.g. 3 parts by mass) at the silica surface, a proportion of silanol groups during modification underwent condensation with silane molecules. Formation of siloxane bonds resulted in stable binding of silane with the silica surface. The reaction course was as follows (Scheme 2).

When a higher amount of silane was used in the modifying solution (e.g. 5 parts by mass), more surface silanol groups became condensed with molecules of the hydrolysed silane. The course of the reaction could run as follows (Scheme 3).

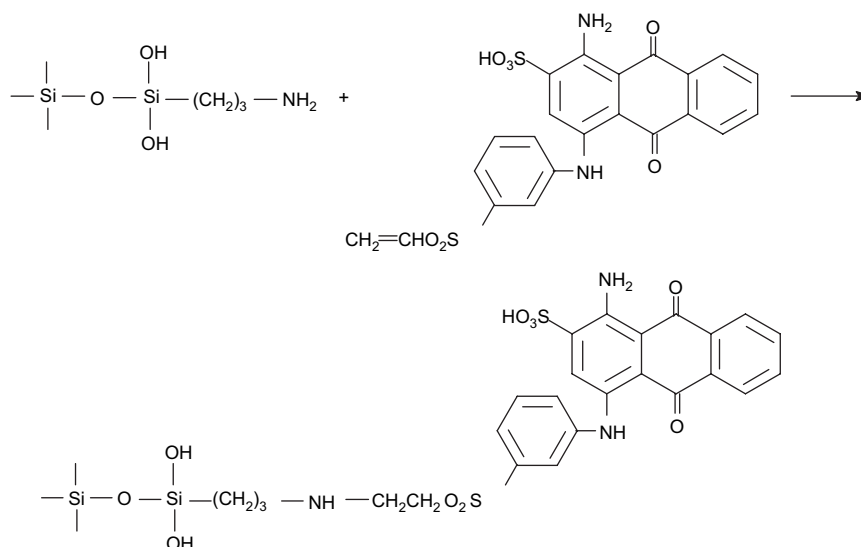
Extents of removal of C.I. Reactive Blue 19 dye from waste solution following adsorption on the silica modified with 3 or 5 parts of silane U-13 in various solvents and, for comparison, on the unmodified silica are presented in Table 2.

When unmodified silica was used for adsorption, the extent of dye removal from the solution was low and never exceeded 4%.

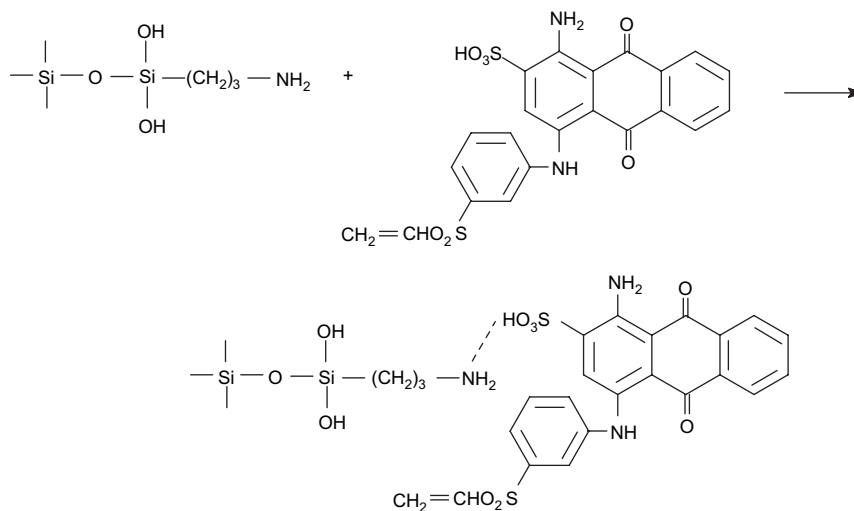
The application of aminosilane U-13 for silica surface modification clearly improved the extent of dye removal from



Scheme 4.



Scheme 5.



Scheme 6.

solution. Thus, silica surface modification favourably affected adsorptive properties of the silica. In the adsorption, application of silica modified with 3 parts of aminosilane in every case augmented the extent of dye removal to over 90% and a solvent used for modification exerted insignificant effect on the improved dye removal from the solution by adsorption. By employing higher amounts of the adsorbent, a further increase in dye removal from the solution could be obtained. The best adsorbents included samples 25 RB I-3-2 and 25 RB III-3-2, which removed as much as 99.6% of the dye. Silica modified with 5 parts of aminosilane manifested a slightly higher extent of dye removal (up to 100%), as compared to that secured by the silica modified with 3 parts of U-13 aminosilane. The least efficient adsorbent was sample 25 RB II-5-1 (the extent of dye removal: 87.6%).

The extent of C.I. Reactive Blue 19 dye removal from a solution of 50 mg dm^{-3} concentration following adsorption

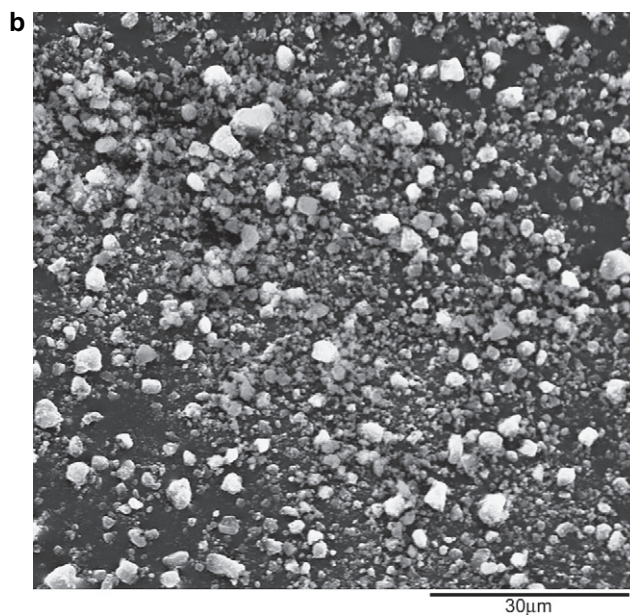
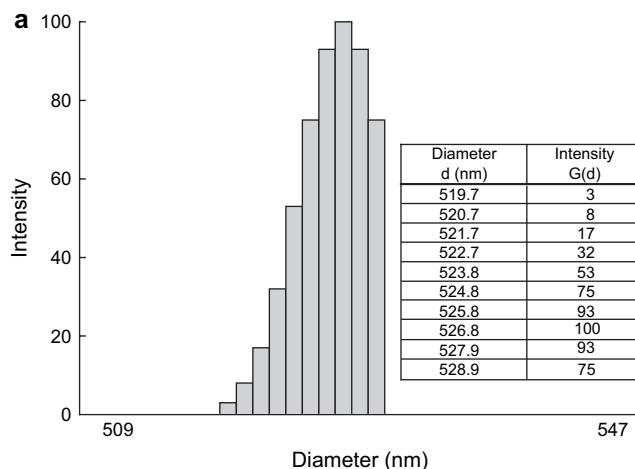


Fig. 1. Multimodal particle size distribution (a) and SEM micrograph (b) of unmodified silica Syloid® 244.

Table 5

Oil number, mean particle diameter and polydispersity of pigments

Symbol of sample	Oil number ($\text{cm}^3 \times 100 \text{ g}^{-1}$)	Mean particle diameter (nm)	Polydispersity
25 RB III-5-2	372.0	798	0.062
25 RB I-5-2	372.0	714	0.003
25 RB I-5-3	418.5	428	0.030
25 RB IV-5-2	325.5	825	0.197
25 RB IV-5-3	325.5	1430	0.202
25 RB IV-5-4	279.0	564	0.102
50 RB I-5-1	325.5	782	0.241
50 RB I-5-2	325.5	835	0.254
50 RB I-5-3	279.0	857	0.239
50 RB I-3-1	325.5	1151	0.266
50 RB I-3-2	279.0	1284	0.295
50 RB I-3-3	325.5	939	0.258
50 RB V-5-2	279.0	914	0.229
50 RB V-5-3	279.0	1123	0.248
50 RB IV-5-2	372.0	800	0.271
300 RB I-5-2	372.0	642	0.182
300 RB I-5-3	372.0	589	0.258

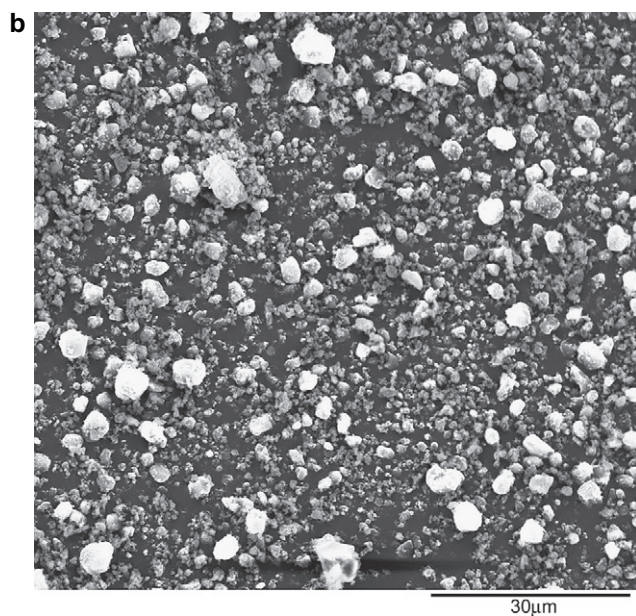
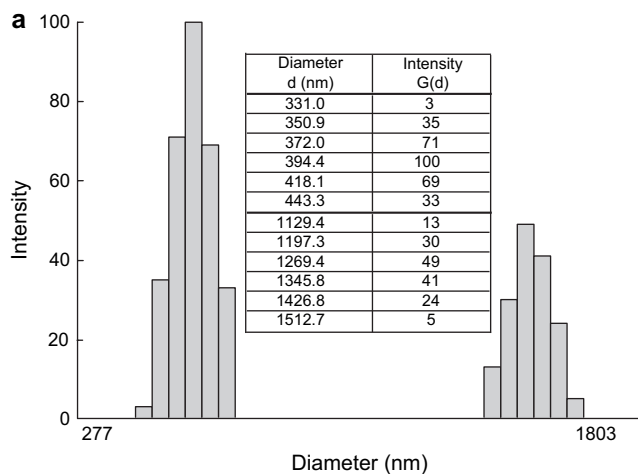


Fig. 2. Multimodal particle size distribution (a) and SEM micrograph (b) of Syloid® 244 silica modified with 5 parts by weight U-13 silane.

with silica modified with 3 or 5 parts of U-13 silane in selected solvents is presented in Table 3.

Despite the elevated dye concentration in the purified solution, the extent of dye removal was very high (98–100%). Also in this case, application of silicas modified with 5 parts of aminosilane resulted in more pronounced removal of the dye from solution. Also the use of increased amounts of the silica promoted a more complete dye removal or more extensive purification of the waste solution.

Results of purification of waste solution containing 300 mg dm^{-3} of the organic dye are presented in Table 4.

At a dye concentration of 300 mg dm^{-3} optimum results were obtained for adsorption of the dye using 3 g of the silica, which had been modified in toluene with 5 parts of U-13 aminosilane (the extent of dye removal: 99.7%). The test was slightly less advantageous when 2 g of silica was applied (the extent of dye removal: 99.3%).

Selected pigments were subjected to dye desorption from the silica surface. Analysis of the results demonstrated that

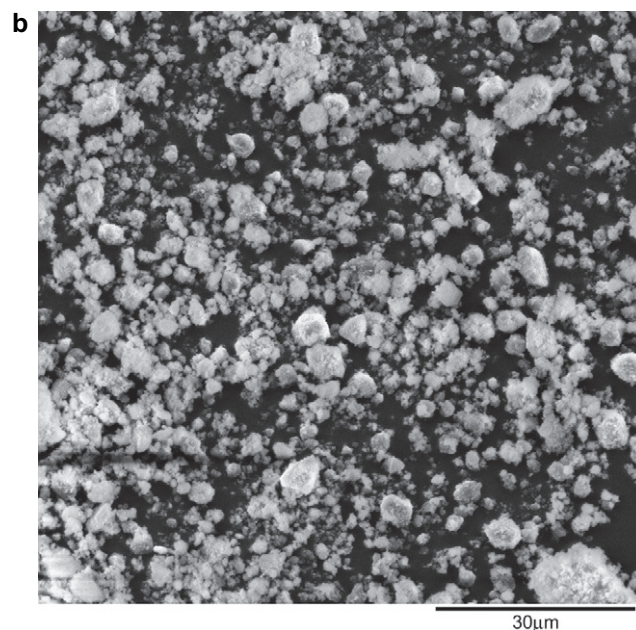
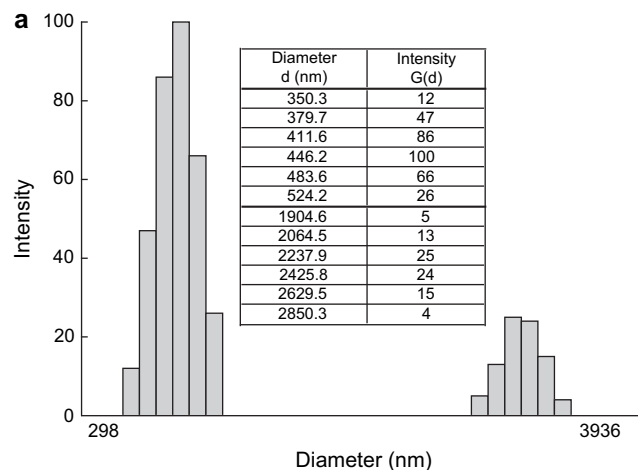


Fig. 3. Multimodal particle size distribution (a) and SEM micrograph (b) of pigment 25 RB IV-5-2.

in practice no desorption of the dye adsorbed at the silica surface took place. This might indicate that strong chemical bonds stabilize the organic dye on the modified silica adsorbent. Only in two of the examined samples slight desorption of the dye took place from the pigment surface (5–7%).

The probable mechanism of binding C.I. Reactive Blue 19 to the surface of the aminosilane-modified silica is suggested in Schemes 4 and 5, consistent with the absence or very low desorption of the dye from the surface of silica carrier. Only in two cases a very small amount of the dye was removed from the silica surface, which might point to interactions involving hydrogen bonds. On the other hand, for most of the pigments the stability of the dye–SiO₂ surface bond was most positive. This may provide rationale for the notion that adsorption of the dye on silica resulted in a stable chemical covalent bond (Scheme 5).

In the first stage, the mechanism may involve transformation of the β-sulphatethylsulphonic group, SO₂CH₂CH₂OSO₃Na of

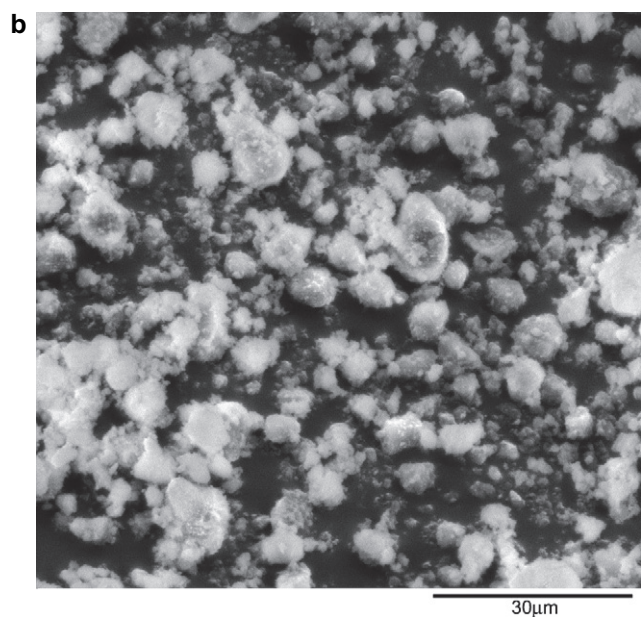
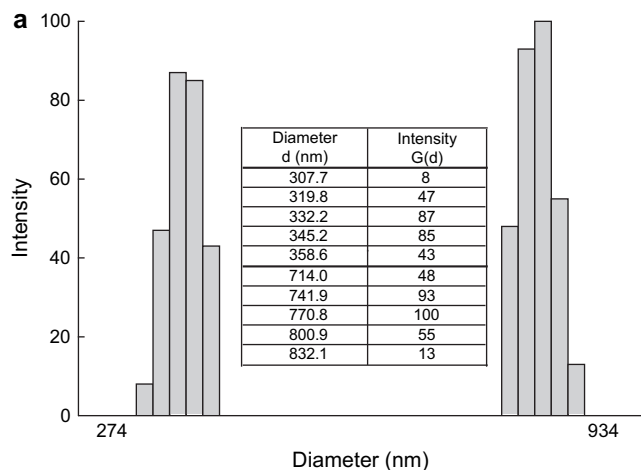


Fig. 4. Multimodal particle size distribution (a) and SEM micrograph (b) of pigment 25 RB IV-5-4.

the dye into vinylsulphonic group, $-\text{SO}_2\text{CH}=\text{CH}_2$. Under alkaline conditions, the group splits off sulphate residue, as follows (Scheme 4):

Subsequently, the so formed vinylsulphonic group may interact with the modified silica surface forming a covalent bond (Scheme 5).

In turn, hydrogen bonds may form between nitrogen atom of the modified silica amine group and hydrogen atom of the organic dye sulphonic group (Scheme 6).

The characteristics such as oil number, mean particle diameter and polydispersity of the obtained pigments are listed in Table 5.

Values of oil numbers ranged from $93 \text{ cm}^3 \times 100 \text{ g}^{-1}$ for pure C.I. Reactive Blue 19 dye to $418.5 \text{ cm}^3 \times 100 \text{ g}^{-1}$ for the pigment obtained by dye adsorption on the silica surface modified with 5 weight parts of U-13 (solvent: toluene).

Particle size distribution for the unmodified silica is presented in Fig. 1a. The narrow band of primary agglomerates could be noted in the range of 520–530 nm (maximum

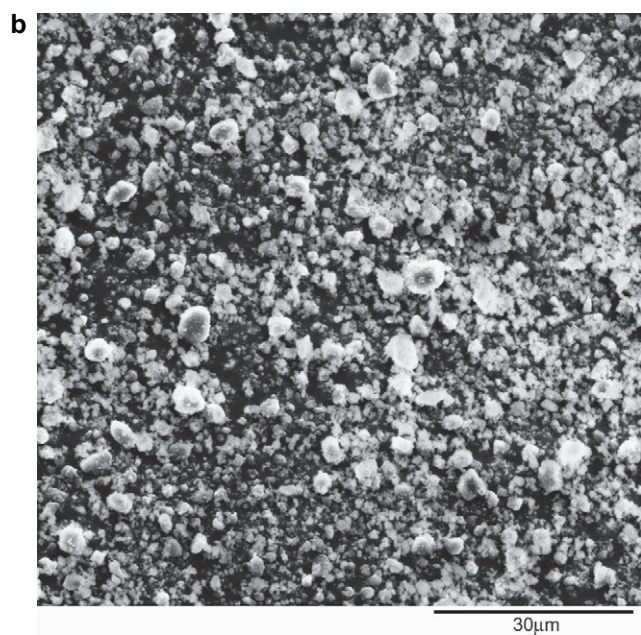
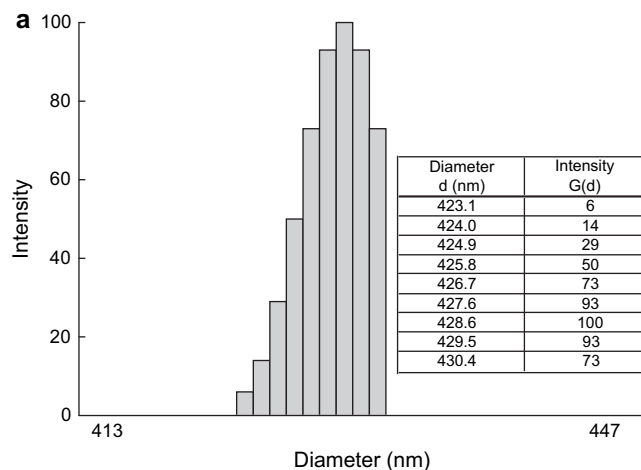


Fig. 5. Multimodal particle size distribution (a) and SEM micrograph (b) of pigment 25 RB I-5-3.

intensity of 100 corresponded to particles of 526.8 nm in diameter). Polydispersity of the silica amounted to 0.005, and the mean particle diameter was 526 nm. The silica was uniform, as confirmed by microscopy (Fig. 1b).

In the particle size distribution of the silica modified with 5 weight parts of aminosilane in toluene (Fig. 2a) two bands of agglomerates could be noted. The band of primary agglomerates fitted the range of 331–443 nm (maximum intensity of 100 corresponded to particles of 394.4 nm in diameter) while the less intense band of secondary agglomerates was present within the range of 1129–1513 nm. Polydispersity amounted to 0.183 and the mean particle diameter was 703 nm. Thus, coating of silica with the dye produced a pigment of favourable parameters.

Pigment 25 RB IV-5-2, represented by Fig. 3a and b, showed the presence of both primary and secondary agglomerates.

In Fig. 3a, the intense band in the range of 350–524 nm (maximum intensity of 100 corresponded to particles of

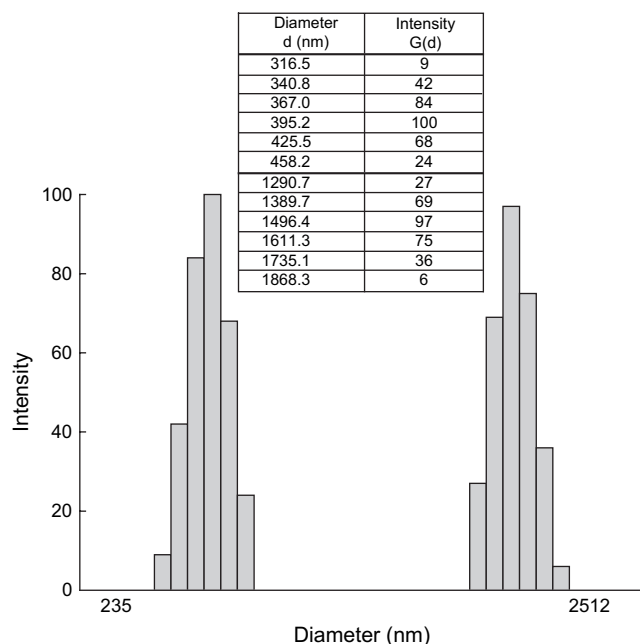


Fig. 6. Multimodal particle size distribution of pigment 50 RB I-3-3.

446.2 nm in diameter) represented primary agglomerates while the band of low intensity in the range of 1905–2850 nm corresponded to secondary agglomerates (maximum intensity of 25 corresponded to particle diameter of 2237.9 nm). Polydispersity of the pigment reached 0.197 while the mean particle diameter was as high as 825 nm. In this case, the presence of secondary agglomerates was reflected by unfavourably augmented polydispersity. Micrograph confirmed the presence of smaller primary agglomerates and larger structures of secondary agglomerates (Fig. 3b).

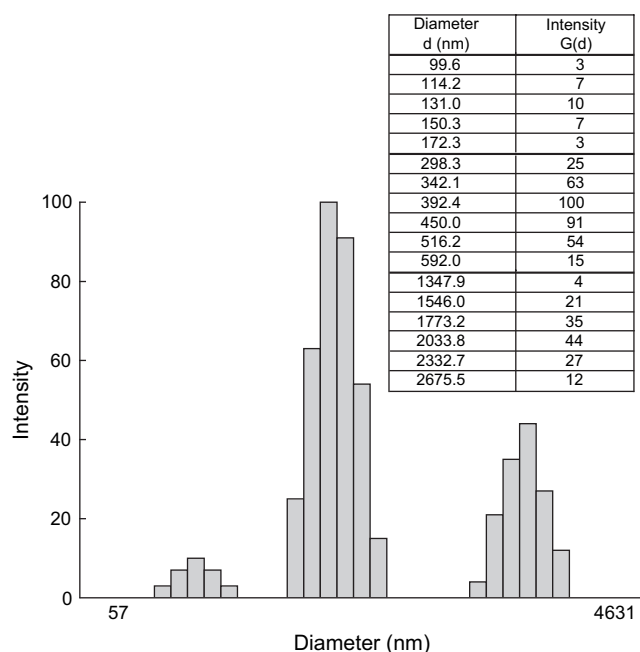


Fig. 7. Multimodal particle size distribution of pigment 50 RB I-5-2.

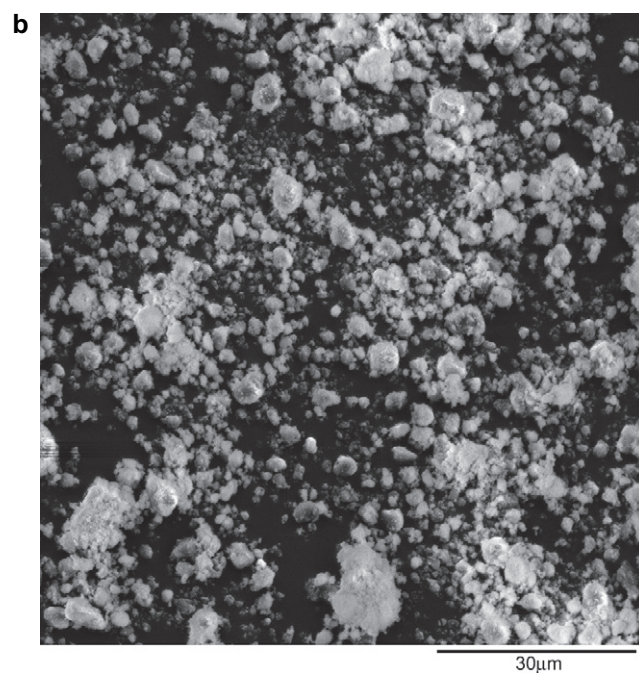
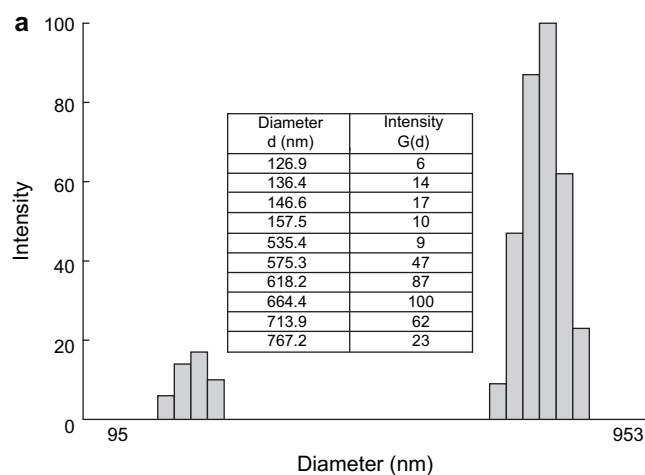


Fig. 8. Multimodal particle size distribution (a) and SEM micrograph (b) of pigment 300 RB I-5-3.

In the case of the 25 RB IV-5-4 pigment, the particle size distribution (Fig. 4a) demonstrated the presence of two bands of aggregates: the less intense one in the diameter range of 308–359 nm (maximum intensity of 87 corresponded to particle diameter of 332.2 nm) and the more intense one in the

Table 6

Physicochemical parameters of acrylic paint (AKRYBET)

Parameter	AKRYBET	AKRYBET with 0.025 RB I-5-3 pigment
Density (g cm ⁻³)	1.30	1.20
Viscosity KW 10 estimated by time of dripping (s)	Drips after 50–150	Drips after 60
Drying time		
First stage (min)	50	40
Second stage (min)	54	48
Resistance to wet scrubbing	Base exposure after 1500 advances	Base exposure after 12,000 advances

range of 714–832 nm (maximum intensity of 100 corresponded to the particle diameter of 770.8 nm). Polydispersity amounted to 0.102 and mean particle diameter was 564 nm. The structures could easily be noted in the micrograph (Fig. 4b).

Particle size distribution in the 25 RB I-5-3 pigment is shown in Fig. 5a.

In the distribution, a single band representing primary agglomerates (aggregates) fitted the very narrow range of 423–430 nm (maximum intensity of 100 corresponded to particles of 428.6 nm in diameter). The pigment showed very uniform particles, which was reflected by polydispersity value of 0.030 and confirmed by SEM micrograph (Fig. 5b). The mean aggregate diameter was as low as 428 nm.

Particle size distribution for the 50 RB I-3-3 pigment (Fig. 6) manifested the first band of primary agglomerates in the range of 316–458 nm (maximum intensity of 100 corresponded to the particle diameter of 395.2 nm). The other band, representing secondary agglomerates, was present in the range of 1291–1868 nm (maximum intensity of 97 corresponded to the particle diameter of 1496.4 nm). Polydispersity proved to be rather high and amounted to 0.258. This certainly reflected the presence of secondary agglomerates, which negatively affected the structure and homogeneity of the pigment. In this case, the mean particle diameter was very high (939 nm).

In the case of 50 RB I-5-2 pigment, the particle size distribution (Fig. 7) manifested the presence of three bands.

Two of the bands corresponded to aggregates (primary agglomerates). The first band of low intensity fitted the range of 100–172 nm (maximum intensity of 10 corresponded to the particle diameter of 131.0 nm). The other band was noted in the diameter range of 298–592 nm (maximum intensity of 100 corresponded to the aggregate diameter of 392.4 nm). The third band, reflecting the presence of secondary agglomerates, was noted in the range of 1348–2676 nm (maximum intensity of 44 corresponded to the particle diameter of 2033.8 nm). The mean diameter of the particles was 835 nm, and the polydispersity amounted to 0.254.

The 300 RB I-5-3 pigment demonstrated the presence of two bands (Fig. 8a). The band of low intensity, within the diameters of 127–158 nm (maximum intensity of 17 corresponded to the particle diameter of 146.6 nm) represented primary particles of the pigment. Their presence argued for a particular value of the obtained pigment. However, primary agglomerates were present also in the diameter range of 535–767 nm (maximum intensity of 100 corresponded to the agglomerate diameter of 664.4 nm), affecting to certain extent properties of the pigment, i.e. decreasing its value. The respective electron micrograph (Fig. 8b) documented numerous primary particles of the pigment but also the presence of larger particle groups, linked into primary agglomerates.

Results of tests performed on the dispersive acrylic paint for exterior use, AKRYBET, containing the 25 RB I-5-3

pigment and the most favourable physicochemical parameters, are presented in Table 6.

The coat obtained following application of the studied AKRYBET paint demonstrated excellent resistance for wet scrubbing as well as a good quality coating. Studies on the extent of drying and drying time showed that the first stage of desiccation was reached after 40 min and the second stage after 48 min. The tests for adherence to bed showed no tearing of the incised coat margins. Moreover, the obtained paint posed no problems upon brush application.

4. Conclusions

The results show that the aminosilane-modified silica could be used as a selective adsorbent in the purification of waste dye solutions; its application secured highly efficient removal of dye (in most cases over 90% and in some cases even 100%). The silica-carrier product could then be used as a pigment within an exterior acrylic paint. Optimum properties were obtained using 5% silane; the ensuing pigment displayed very low polydispersity (0.030), low mean particle diameter (428 nm) and no tendency to form secondary agglomerates.

Acknowledgement

This work was supported by the Poznan University of Technology Research Grant BW No. 32/117/2004.

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