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ADSORPTION OF C.I. BASIC BLUE 9 ONTO TiO₂–SiO₂ INORGANIC SUPPORT

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Abstract. Adsorption of C.I. Basic Blue 9 (Methylene Blue Hydrate) on the surface of TiO₂–SiO₂ oxide composite unmodified or functionalized with N-2-(aminoethyl)-3-amino propyltrimethoxysilane was investigated. The organic dye was supported on inorganic TiO₂–SiO₂ oxide composite precipitated in the emulsion system. The process of adsorption was performed for the dye concentrations from 100 to 3000 mg/dm³. Specific surface area of support was determined prior to and after modification with aminosilane. The pigments obtained were subjected to characterization of their physicochemical properties, including particle size distributions and surface morphology as well as colorimetric analysis. Elemental analysis allowed evaluation of the degree of support coverage with the dye. The data obtained permitted assessment of the pigments quality and the effectiveness of support surface modification.

keywords: TiO₂–SiO₂ oxide composite, emulsion precipitation, adsorption, C.I. Basic Blue 9, pigments, morphological properties

1. Introduction

At many research groups intense investigation is carried out aimed at obtaining of inorganic fillers characterized with relatively high surface activity, based on activated carbon, SiO₂, TiO₂, Al₂O₃, MgO, MgSiO₃ etc. (Malik 2002; Wu 2006; Jesionowski 2009a, 2009b; Siwinska-Stefanska 2010; Ciesielczyk 2011; Pilarska 2011).

Titanium dioxide is well known not only as a filler or support but also as a photocatalyst used in the processes of air or wastewater purification (Cho 2008). TiO₂ exists in three crystallographic forms of anatase, rutile and brookite. To improve its properties suitable for particular application as a component of paints or cosmetic products, its surface is covered with a layer of inert oxide (e.g. SiO₂) to make a composite containing a ≡Ti–O–Si≡ bond.

Most often produced inorganic oxides are titanium-silica ($\text{TiO}_2\text{-SiO}_2$), titanium-zirconium ($\text{TiO}_2\text{-ZrO}_2$) and titanium-aluminium ($\text{TiO}_2\text{-Al}_2\text{O}_3$) oxide composites. Coverage of titanium core with a silica layer can reduce the photocatalytic properties of TiO_2 , while addition of silicon dioxide increases TiO_2 resistance to atmospheric elements and facilitates dispersion in liquids.

Many methods for the synthesis of titania-silica composite have been proposed, including the sol-gel method (Dutoit 1995) and chemical precipitation method (Liu 2008). Recently an interesting proposed method is the synthesis of $\text{TiO}_2\text{-SiO}_2$ from emulsion system using solutions of sodium silicate and titanium sulphate as Si and Ti precursors, and an organic solvent has been performed (Siwinska-Stefanska 2010).

Among others, titania-silica support has been used for adsorption of dyes to get hybrid pigments of widespread use in food and cosmetic industry, in production of lacquers, etc. The pigments have been also employed for colouration of plastics, while in food industry for colouration of food products and drinks, and in pharmaceutical industry for colouration of drugs and tablets. The pigments are also used for colouration of paper. The above examples illustrate the wide range of pigments application. They are met in almost all spheres of everyday life and thanks to the use of new technologies they have become more environmentally friendly.

Adsorption of organic dyes on the surface of $\text{TiO}_2\text{-SiO}_2$ composite can be performed by many methods (Messina 2006). For example it can be carried out in a special reactor at a controlled temperature or on titanium dioxide modified with aminosilane. In another method the dyes (C.I. Reactive Blue 19 and C.I. Acid Orange 7) have been adsorbed by introducing a water solution of the dye onto unmodified or modified titanium dioxide (Andrzejewska 2004). Different dyes (cationic and anionic) have been adsorbed on unmodified $\text{TiO}_2\text{-SiO}_2$ composite at different pH of the reaction environment (Park 2007). The yield of adsorption and its character have been found to depend on the surface charge of the $\text{TiO}_2\text{-SiO}_2$ composite. At $\text{pH}>3$ the surface of the support is negatively charged, while at $\text{pH}<3$ positively. For a negatively charged surface the adsorption of anionic dyes is less effective than cationic ones, while a positively charged surface the adsorption of anionic dyes is more effective.

The study presented was aimed at synthesis of hybrid pigments by adsorption of C.I. Basic Blue 9 organic dye on the surface of inorganic support $\text{TiO}_2\text{-SiO}_2$ unmodified or functionalized with aminosilane U-15D. Moreover, the effect of the support's surface modification on the physicochemical properties of the pigments obtained was established.

2. Experimental

$\text{TiO}_2\text{-SiO}_2$ oxide composite was synthesised by emulsion precipitation method using solutions of sodium silicate and titanium sulphate as precursors of silica and titanium dioxides, moreover the organic solvent (cyclohexane) was used. The precipitated composite was calcined at 950°C for 2 hours to get the rutile form of

titanium dioxide. The TiO₂-SiO₂ hybrid system obtained was modified with 3 wt./wt. of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D), made by Unisil. The modification was performed in a reactor of 0.5 dm³ in capacity, charged with 20 g of the hybrid system and a solution of U-15D in an appropriate volume of the solvent composed of water and methanol at the 1:4 volume ratio. The choice of modifier was made on the basis of earlier studies (Jesionowski 2002, 2003; Andrzejewska 2004). The amine groups from silane are needed to form stable chemical bond with the dye adsorbed. Functionalization of titanium dioxide support with U-15D has been reported to significantly increase the yield of adsorption (Andrzejewska 2004; Jesionowski 2008). The modification process was detailed described by Jesionowski et al. (2000).

The C.I. Basic Blue 9 dye used to obtain the studied pigments was purchased from Sigma-Aldrich. The process of adsorption was carried out in a reactor containing 7.5 g of unmodified or functionalized hybrid oxide to which 250 cm³ of a water solution of the dye in appropriate concentration was added. The suspension was stirred for 2 hours with a R05 magnetic stirrer made by IKA Werke GmbH. Then, the whole system was filtered off under reduced pressure, the filtrate was dried by the convection method at 105°C. The TiO₂-SiO₂ hybrid system precipitated and the pigments obtained were characterized by a thorough physicochemical analysis.

Particle size distributions of the hybrid system and pigments obtained were determined with the use of a Zetasizer Nano ZS working on the basis of non-invasive backscattering method (NIBS) made by Malvern Instruments Ltd. The degree of dispersion and morphology of the products were evaluated by a scanning electron microscope (Zeiss VO40). Crystalline structure of TiO₂-SiO₂ was determined by the X-Ray diffraction method (WAXS) using a TUR-M62 diffractometer. Hydrophilic/hydrophobic properties of the samples studied were evaluated by a K100 tensiometer made by Krüss, on the basis of capillary penetration of water in the samples. Adsorption properties of selected samples were characterized by determination of their specific surface area using an ASAP 2020 instrument made by Micromeritics Instrument Co. Chemical analysis of the products was performed on an Elemental apparatus, model Vario EL Cube. Colorimetric characterization of the samples was made using the CIE L*a*b* system on a SPECBOS 4000 colorimeter (made by YETI Technische Instrumente GmbH). The results are given in the CIE L*a*b* system, where: L* – lightness, +a* – contribution of red colour, -a* – contribution of green colour, +b* – contribution of yellow colour, -b* – contribution of blue colour, also colour saturation – C* and total change in colour – ΔE*.

3. Results and discussion

In the first stage of the study, the TiO₂-SiO₂ oxide hybrid unmodified and modified with 3 wt./wt. of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane was subjected to dispersive and morphological analysis. The particle size distribution of unmodified TiO₂-SiO₂ shows a single band covering the range of diameters from 459 to 1110 nm (Fig. 1). An analogous distribution of TiO₂-SiO₂ subjected to surface modification

with aminosilane has two bands covering the ranges from 342 to 1720 nm and from 3580 to 6440 nm. A comparison of the particle size distributions obtained for these two samples reveals that the modification brings about the appearance of a band corresponding to secondary agglomerates. The polydispersity index of $\text{TiO}_2\text{-SiO}_2$ unmodified and grafted with U-15D is 0.375 and 0.314, respectively. The particles in both samples show a tendency towards formation of agglomerates of approximately spherical shape. The modified sample is a bit less uniform, which follows from a greater tendency of its particles to agglomerate. The SEM images (Fig. 2a and 2b) confirm the presence of secondary agglomerates.

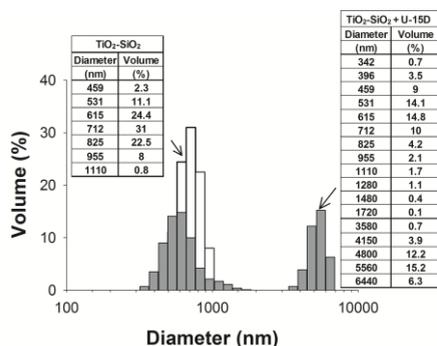


Fig. 1. Comparison of particle size distributions according to volume contributions of unmodified and modified $\text{TiO}_2\text{-SiO}_2$

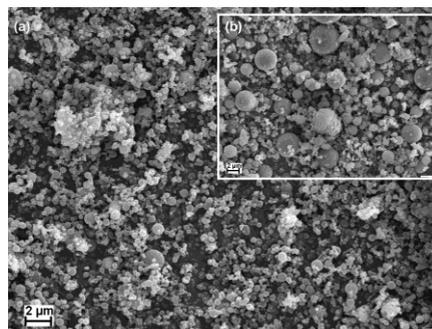


Fig. 2. SEM images of $\text{TiO}_2\text{-SiO}_2$ (a) unmodified and (b) modified

The studies were planned to be performed on $\text{TiO}_2\text{-SiO}_2$ with titanium dioxide of rutile structure because this crystalline form is highly stable and does not induce photocatalytic destruction of the dye. As follows from XRD measurements, titanium dioxide of rutile form gives intensity peaks at 2θ of 27.45, 36.08, 39.18, 41.22, 44.05, 54.32 and 56.64, while that of anatase variety gives peaks at 2θ of 25.28, 32, 33, 33.50, 48.05 and 55.06 (Siwinska-Stefanska 2010; Valverde-Aguilar 2011). According to the diffractogram shown in Fig. 3, the $\text{TiO}_2\text{-SiO}_2$ composite synthesized is mainly composed of the rutile form of TiO_2 (the presence of a low contribution of the anatase variety is indicated by the diffraction maximum at 2θ of 25.28).

The next stage of our study was concerned with assessment of the effect of composite surface modification with U-15D on the hydrophilic/hydrophobic as well as adsorptive properties. The profiles of wettability with water recorded for the unmodified and modified samples indicated that the functionalization of the composite surface reduced its affinity to water, see Fig. 4. The increase in mass of the modified sample was smaller than that of the unmodified one, which proves that the surface functionalization leads the sample more hydrophobic.

Adsorption capacity of the samples was determined by recording nitrogen adsorption/desorption isotherms (Fig. 5) showing that the amount of nitrogen adsorbed by the modified sample was smaller. The specific surface area increased from $3.4 \text{ m}^2/\text{g}$

for the unmodified sample to $5.4 \text{ m}^2/\text{g}$ for the modified one, but the pore volume (V_p) and the mean pore diameter (S_p) decreased for the modified sample (see Table 1).

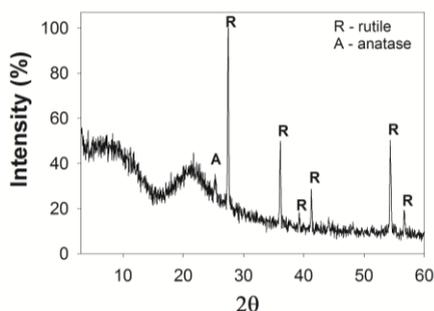


Fig. 3. X-Ray diffractogram of the $\text{TiO}_2\text{-SiO}_2$ support

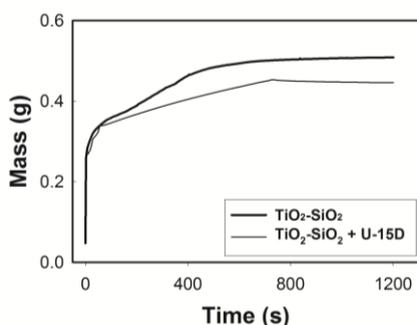


Fig. 4. Profiles of wettability with water recorded for unmodified and modified (3 wt./wt. of U-15D) $\text{TiO}_2\text{-SiO}_2$ composite

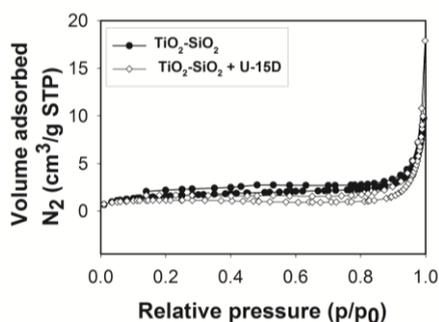


Fig. 5. Nitrogen adsorption/desorption isotherms for unmodified and modified $\text{TiO}_2\text{-SiO}_2$ composites

Table 1. Adsorptive properties of the modified and unmodified $\text{TiO}_2\text{-SiO}_2$ supports used in adsorption of C.I. Basic Blue 9

adsorptive properties	$\text{TiO}_2\text{-SiO}_2$	$\text{TiO}_2\text{-SiO}_2 + \text{U-15D}$
surface area, A_{BET} (m^2/g)	3.4	5.4
total volume of pores, V_p (cm^3/g)	0.015	0.011
mean size of pores, S_p (nm)	13.3	8.1

The pigments obtained in this study can be applied, e.g. in production of paints. For this application very important is the shape and size of pigment particles determining the rheological properties of the paint, hue, resistance to atmospheric elements and easy dispersion. Usually the pigment particles diameters are in the range from 1 to $10 \mu\text{m}$. If pigment particles represent a variety of sizes, the coat of paint will be more resistant to atmospheric elements. Therefore, from the point of view of this application, the dispersive and morphological characterization of pigments is very important. The relevant physicochemical analyses have been rather broadly presented in literature (Binkowski, 2000; Andrzejewska, 2007). The use of $\text{TiO}_2\text{-SiO}_2$ composite precipitated in emulsion system as a support of organic dyes, gave pigments of

particles of spherical shape and much smaller diameters than those met in other commonly used pigments based on other types of supports. The use of the functionalized $\text{TiO}_2\text{-SiO}_2$ as a support of the organic dye studied led to pigments of diameters smaller than those in the pigments based on unmodified support. The particle size distributions according to volume contribution obtained for the pigments prepared by adsorption of C.I. Basic Blue 9 in concentrations of 500 or 3000 mg/dm^3 on unmodified $\text{TiO}_2\text{-SiO}_2$ (Fig. 6) visible two bands covering the diameter ranges 342–955 nm and 255–955 nm. An analogous particle size distribution for the pigment obtained by adsorption of C.I. Basic Blue 9 in concentration of 500 mg/dm^3 on the modified support shows a band covering the range 220–712 nm instead of the band covering the range 342–955 nm visible for the unmodified support. A similar shift was observed for the pigment obtained by adsorption of C.I. Basic Blue 9 in concentration of 3000 mg/dm^3 .

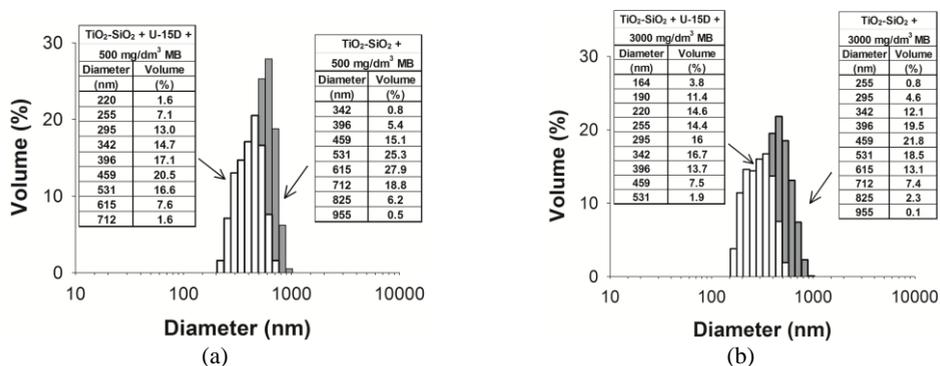


Fig. 6. Comparison of the particle size distributions according to volume contributions evaluated for the pigments obtained by adsorption of C.I. Basic Blue 9 in concentration (a) 500 mg/dm^3 and (b) 3000 mg/dm^3 on unmodified and functionalized $\text{TiO}_2\text{-SiO}_2$ support

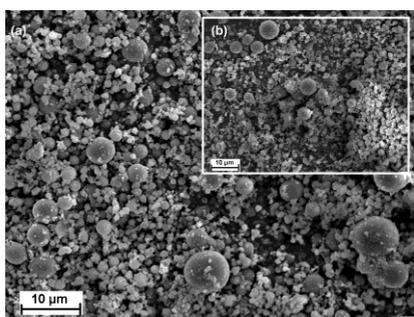


Fig. 7. SEM images of the pigments obtained by adsorption of C.I. Basic Blue 9 in concentration of 3000 mg/dm^3 on (a) unmodified and (b) modified $\text{TiO}_2\text{-SiO}_2$ support

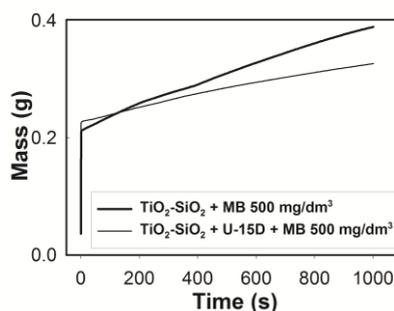


Fig. 8. Profiles of wettability with water estimated for the pigments obtained by adsorption of C.I. Basic Blue 9 in concentration of 500 mg/dm^3 on $\text{TiO}_2\text{-SiO}_2$ and $\text{TiO}_2\text{-SiO}_2 + \text{U-15D}$

Table 2. Elemental content and degree of coverage for the pigments obtained by adsorption of C.I. Basic Blue 9 on unmodified and modified TiO₂-SiO₂ support

Initial dye concentration (mg/dm ³)	TiO ₂ -SiO ₂				TiO ₂ -SiO ₂ + U-15D			
	Content (%)			Degree of coverage (μmol/m ²)	Content (%)			Degree of coverage (μmol/m ²)
	N	C	S		N	C	S	
0	0.003	0.030	0.015	–	0.301	0.346	0.005	–
100	0.015	0.142	0.034	2.16	0.322	0.513	0.026	4.99
500	0.033	0.188	0.036	2.87	0.493	0.521	0.028	5.06
1000	0.036	0.192	0.043	2.93	0.495	0.532	0.031	5.18
1500	0.040	0.208	0.049	3.17	0.498	0.552	0.032	5.37
2000	0.045	0.223	0.056	3.40	0.499	0.559	0.034	5.44
2500	0.049	0.246	0.058	3.76	0.501	0.567	0.038	5.52
3000	0.051	0.258	0.063	3.94	0.505	0.582	0.040	5.67

Table 3. Colorimetric data for the pigments obtained by adsorption of C.I. Basic Blue 9 onto unmodified and functionalized TiO₂-SiO₂ support

Initial dye concentration (mg/dm ³)	TiO ₂ -SiO ₂					TiO ₂ -SiO ₂ + U-15D				
	Colorimetric data									
	L*	a*	b*	C*	ΔE*	L*	a*	b*	C*	ΔE*
0	93.70	0.29	2.76	2.70	–	93.73	0.30	2.68	2.78	–
100	85.41	8.13	-6.34	24.39	41.71	62.14	0.86	-23.00	8.97	15.34
500	78.07	9.53	-12.46	25.39	43.03	61.22	1.43	-23.53	12.54	22.11
1000	77.20	9.13	-13.27	27.84	46.15	59.27	1.95	-26.31	13.04	24.45
1500	75.62	11.04	-14.15	28.77	47.72	57.95	2.73	-26.57	14.95	26.56
2000	72.33	11.61	-15.03	30.55	51.08	55.04	3.01	-28.26	15.66	28.98
2500	70.36	12.10	-15.80	30.97	51.81	54.28	3.58	-28.51	16.20	30.28
3000	67.99	12.05	-18.02	30.36	54.67	53.90	5.32	-28.91	18.79	33.73

The pigment based on unmodified support has particles of diameters from the range 255–955 nm, while that based on functionalized support has particles of diameters shifted towards smaller values – from 164 to 531 nm.

As follows from the SEM images presented in Fig. 7, the pigments based on unmodified TiO₂-SiO₂ support are built of spherical shape particles and show rather low uniformity. Analysis of the wettability profiles with water (Fig. 8) indicates that the mass increase in time for the pigment based on the functionalized support is lower than that for the pigment based on the unmodified support.

The products obtained were also subjected to determination of chemical composition by elemental analysis. As follows from the results presented in Table 2, the content of C, N and S elements increases with increasing initial concentration of the dye, which is related to the degree of coverage. Many authors have used the notion a support degree of coverage with an organic dye for evaluation of the yield of adsorption (Harris, 2001; Jesionowski, 2011). The degree of coverage can be calculated from the expression proposed by Berendsen and de Golan (1978). In our study the degree of coverage increased with increasing initial concentration of the dye. For the pigment obtained by adsorption of C.I. Basic Blue 9 in the initial concentration

of 100 mg/dm^3 the degree of coverage was $2.16 \text{ } \mu\text{mol/m}^2$, while for the initial concentration of the dye of 3000 mg/dm^3 the degree of coverage was $3.94 \text{ } \mu\text{mol/m}^2$. Modification of inorganic support surface with aminosilane (U-15D) causes an increase in this parameter. For the pigment obtained by adsorption of C.I. Basic Blue 9 of the initial concentration of 100 mg/dm^3 on the unmodified support the degree of coverage is $2.16 \text{ } \mu\text{mol/m}^2$, while for that obtained by adsorption of the same dye in the same concentration on the modified support the degree of coverage is $4.99 \text{ } \mu\text{mol/m}^2$. An analogous tendency has been observed for C.I. Basic Red 5 adsorption on the silica support (Jesionowski, 2008).

The effect of $\text{TiO}_2\text{-SiO}_2$ support modification and concentration of the dye on the colour of the pigments obtained was evaluated with the use of the CIE $L^*a^*b^*$ colour space system. According to the data presented in Table 3, the lightness of the products obtained decreases with increasing initial concentration of the dye adsorbed. The greatest total change in colour ΔE^* 54.67 was observed for the pigment obtained by adsorption of C.I. Basic Blue 9 of the initial concentration 3000 mg/dm^3 on the unmodified $\text{TiO}_2\text{-SiO}_2$ support. The total change in colour ΔE^* for the pigment obtained by adsorption of C.I. Basic Blue 9 on the modified $\text{TiO}_2\text{-SiO}_2$ support was much smaller 33.73.

4. Conclusions

The proposed method for the synthesis of $\text{TiO}_2\text{-SiO}_2$ oxide composite by precipitation from emulsion gives products characterized by a monomodal particle size distribution and specific surface area of $3.42 \text{ m}^2/\text{g}$. Functionalization of the composite surface with aminosilane resulted in deterioration of the dispersive and morphological properties but also in specific surface area increase to $5.42 \text{ m}^2/\text{g}$. The pigments obtained on the basis of the functionalized support showed better dispersive properties and more intense colour than those based on the unmodified $\text{TiO}_2\text{-SiO}_2$ support. Surface functionalization of $\text{TiO}_2\text{-SiO}_2$ composite with aminosilane (U-15D) also brought about an increase in the degree of coverage with the dye and gave pigments characterized with a lower affinity to water. Colorimetric analysis of $\text{TiO}_2\text{-SiO}_2$ functionalized with U-15D and the use of this support for adsorption of C.I. Basic Blue 9 proved the greater colour intensity of the pigment obtained then that obtained on unmodified $\text{TiO}_2\text{-SiO}_2$.

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