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Preparation of hybrid pigments via adsorption of selected food dyes onto inorganic oxides based on anatase titanium dioxide

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ABSTRACT

The paper reports on a characterisation of hybrid pigments obtained via adsorption of selected food dyes onto inorganic oxides based on anatase titanium dioxide. The process of adsorption was conducted for dye concentrations varying from 10 to 50 mg/dm^3. The physicochemical properties of the inorganic supports and hybrid pigments obtained were determined. Particle size distribution and surface morphology, and adsorptive as well as electrokinetic properties (zeta potential) of the above products were evaluated. The efficiency of food dye adsorption on TiO_2 or TiO_2–SiO_2 was examined and the degree of coverage of the inorganic supports with the food dyes was also estimated from elemental analysis. The synthesised food dye/titania support hybrids can be used in pharmaceutical products.

1. Introduction

Over recent decades, the synthesis of new-generation hybrid oxide systems has become of great importance to scientific development, especially in chemical technology, materials engineering and environmental protection in a broad sense. Inherent in this important area of scientific research is the synthesis of novel, functionalised inorganic oxides based on titania, and their physicochemical characterisation and application.

The properties of TiO_2 are determined by the morphology of its nanoparticles and size of its crystals as well as its structure, which depend on the choice of method of synthesis. Nanocrystalline particles of TiO_2 are usually obtained by precipitation, the microemulsion method (reverse micelles), the sol-gel method, and hydrothermal crystallisation [1–3]. The search for new wasteless and low-temperature methods for the synthesis of titanium dioxide, in order to improve its physicochemical properties, has been continued for the last few years [4]. Many methods for the synthesis of TiO_2–SiO_2 oxide composites have been proposed, in which different precursors of titania and silica have been used. The best known methods are the sol-gel technique [5–9], solvo- and hydrothermal methods [10–14] and the emulsion precipitation route [15]. Some of the methods proposed produce a TiO_2–SiO_2 nanocomposite made of crystalline titania and amorphous silica.

Titanium dioxide, being nontoxic and compatible with the human skin and mucous membranes, is used in both the pharmaceutical and food processing industries. Modified anatase is used for pharmaceutical purposes more frequently than the rutile variety. Titanium dioxide is primarily used as a white pigment for manufacturing pharmaceutical tablets and drugs, but also as a filler and pigment. Therefore the adsorption of dyes for food and pharmaceuticals on precipitated inorganic supports is a very important problem [16]. Titanium dioxide is not metabolised, and is neutral to the human body and its individual organs. This means it can be safely used in the production of packages which are to be in direct contact with food (bottles, milk boxes, packing foils) and of food products (candies, chewing gums) [17]. Food products are dyed to improve their organoleptic properties. The dyes used for this purpose can be either natural or synthetic. The most popular food dyes include curcumin (E100), riboflavin (E101), cochineal (E120), chlorophyll (E140) and natural carotene (E160a). Dyes are usually added in very small amounts at an early stage of food product manufacture, so they must show high thermal stability and high resistance to acids, oxygen and illumination, and must have a long

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shelf-life. The synthetic dyes admitted for use in food products must be experimentally proven to be nontoxic. The list of synthetic dyes approved for use in food products is continually being shortened [18–21]. Many industries use a variety of dyes to colour their products, including the textiles, rubber, paper, plastics, leather, cosmetics, food and mineral industries [22].

The present study was undertaken mainly to determine how the physicochemical properties of inorganic oxides based on anatase titanium dioxide change as a result of adsorption of selected organic compounds (food dyes – C.I. Food Yellow 4, C.I. Food Blue 5:2 and C.I. Food Red 9). Also the efficiency of the adsorption process was evaluated. Titanium dioxide, TiO_2–SiO_2 and the hybrid pigments obtained were thoroughly characterised, and their dispersive, morphological, adsorptive and electrokinetic properties were determined.

2. Experimental

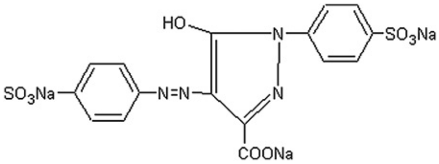
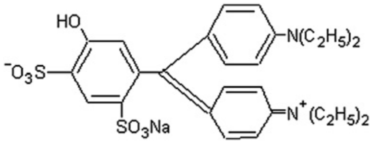
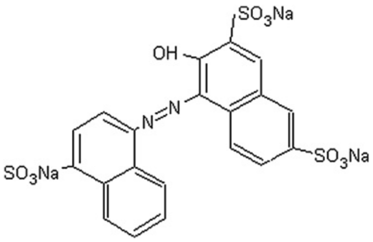
2.1. Methods of obtaining TiO_2 and TiO_2–SiO_2 oxide composite supports

The materials studied were titanium dioxide E171 – commercial pigment made by KRONOS INTERNATIONAL Ltd. – and TiO_2-SiO_2 oxide composite obtained in an emulsion system. KRONOS 1171, admitted as a foodstuff colorant labelled as E171, is an anatase-type pigment with untreated surface, a fine, superwhite powder produced by the sulphate process. In the sulphate method TiO_2 is obtained from ilmenite ore treated with a concentrated solution of sulphuric acid.

The TiO_2–SiO_2 oxide composite was precipitated, using a method proposed by the authors, in an emulsion system with the use of cyclohexane (made by POCh SA, analytical grade) as the organic phase. The titanium precursor was titanium sulphate (made by Chemical Works Police SA) with the following physicochemical parameters: 80–90 g TiO_2/dm^3 concentration, 1250–1270 g/dm^3 density, and $pH < 1$. The precursor of Si was a 5% aqueous solution of sodium silicate (technically filtered water glass, made by Vitrosilicon SA) containing 27.18% SiO_2 and 8.5% Na_2O and of 1390 g/dm^3 density. The emulsifiers were nonylphenylpolyoxyethyleneglycol ethers ($C_9H_{19}PhO(CH_2CH_2O)_nH$) with mean oxyethylenation extent 3 (NP3) and 6 (NP6), purchased from Sigma–Aldrich. Two emulsions were prepared as substrates for the synthesis of TiO_2–SiO_2 oxide composite. Emulsion E1 (alkaline) was obtained from a 5% (expressed in terms of SiO_2 content) aqueous solution of sodium silicate. The water solution of sodium silicate was introduced into the organic phase (cyclohexane). Emulsion E2 (the acidic one) contained titanium sulphate. The organic phase was cyclohexane (titanium sulphate was introduced into cyclohexane). A similar mixture of polyoxyethylenated nonylphenols, but in different proportions, was used as an emulsifier. Prior to the introduction, the titanium sulphate solution was centrifuged in a high-speed Eppendorf Centrifuge 5804. Emulsion E2 was placed in the reactor, into which emulsion E1 was added in doses. Emulsion E2 was vigorously stirred in a T25 Basic type homogeniser (IKA Werke GmbH), running at 16 000 rpm. Upon homogenisation the precipitating agent – sodium silicate in emulsion E1 – was introduced into the reactor at a constant rate of 5 cm^3/min with an ISM833A peristaltic pump (Ismatec). When the dosing of emulsion E1 was complete, the reactive mixture was heated to a temperature of 80 °C to destabilise the emulsion mixture. Subsequently the solvent (cyclohexane) was distilled off. The next stage involved filtration of the mixture under reduced pressure. The sample obtained in this way was washed with distilled water [23]. Finally the sample was dried at a temperature of 105 °C for 18 h, and then calcined at 600 °C for 1 h (Lenton Furnaces type AWF 115/5).

The efficiency of food dye adsorption was compared for the commercial TiO_2 and the precipitated TiO_2–SiO_2 oxide composite. TiO_2–SiO_2 was selected because of its high surface area, determined by the presence of silica, and its higher capacity for adsorption of organic compounds than TiO_2. The process of adsorption significantly depends on the specific surface area and porosity of the adsorbents.

Table 1
Characterisation of the food dyes used.

Food dye	Structure	Formula	Molecular weight (g/mol)	λ_{max} (nm)
C.I. Food Yellow 4		$C_{16}H_9N_4Na_3O_9S_2$	534	426
C.I. Food Blue 5:2		$C_{27}H_{31}N_2O_7S_2Na$	582	638
C.I. Food Red 9		$C_{20}H_{11}N_2Na_3O_{10}S_3$	604	520

2.2. Preparation of hybrid pigments

The hybrid pigments were obtained using selected food dyes (C.I. Food Yellow 4, C.I. Food Blue 5:2 and C.I. Food Red 9) purchased from UNIVAR Ltd. (Table 1), without further purification. All food dyes used were acidic.

To the reactor containing 10.0 g of TiO_2 or TiO_2–SiO_2 support, a portion of 250 cm^3 of aqueous solution of a selected food dye in appropriate concentration was added (solutions were prepared with the following dye concentrations: 10, 15, 20, 25, 30, 35, 40, 45 and 50 mg/dm^3). The suspension was stirred for 1 h with an IKAMAG R05 magnetic stirrer made by IKA Werke GmbH, and then it was filtered off under reduced pressure and the washed sediment was dried in a stationary drier for 24 h, at 105 °C. In the filtrate the concentration of unadsorbed dye was determined by absorbance measurements using an SPECOL UV-1201 spectrophotometer (Shimadzu).

The next step was the evaluation of the hybrid pigments' stability (elution tests). To a conical flask of 200 cm^3 capacity, containing 50 cm^3 water, a portion of 2.5 g of the obtained hybrid pigment was added. The suspension was mixed with an IKAMAG R05 magnetic stirrer (IKA Werke GmbH) for 1 h at room temperature. The suspension was filtered off under reduced pressure. In the filtrate the concentration of the soluble components was evaluated by absorbance measurements on the SPECOL UV-1201 spectrophotometer. The concentration of the eluted dye was read off from the calibration curve.

2.3. Evaluation of physicochemical properties

Determination of certain physicochemical parameters was undertaken to evaluate the yield of adsorption of selected food dyes on the surface of inorganic oxide systems based on TiO_2. Samples of TiO_2 and TiO_2–SiO_2 oxide composite were analysed to determine the particle size distribution and polydispersity index (using a non-invasive back scattering method, Zetasizer Nano ZS, Malvern Instruments Ltd., measuring particles with sizes from 0.6 to 6 000 nm).

The samples of TiO_2 and TiO_2–SiO_2 and randomly selected hybrid pigments were also subjected to morphological and microstructural analysis using a EVO40 scanning electron microscope (Zeiss). The observations permitted evaluation of the degree of dispersion, the structure of the particles, and their tendency to undergo aggregation or agglomeration.

In order to characterise the adsorptive properties, nitrogen adsorption/desorption isotherms at 77 K and parameters such as surface area (A_{BET}), total volume (V_p) and mean size (S_p) of pores were determined using an ASAP 2020 instrument (Micromeritics Instrument Co.). All samples were degassed at 120 °C for 4 h prior to measurement. The surface area was determined by the multi-pointBET (Brunauer–Emmett–Teller) method using the adsorption data as a function of relative pressure (p/p_0). The BJH (Barrett–Joyner–Halenda) method was applied to determine the pore volume and the average pore size.

The TiO_2 and TiO_2–SiO_2 oxide composite were also subjected to crystal structure determination using a WAXS (wide angle X-ray scattering) method. X-ray diffraction measurements were performed using Cu Kα (λ = 1.54056 Å) radiation. The accelerating voltage and the applied current were 30 kV and 15 mA, respectively. The samples were scanned at a rate of 0.04° over an angular range of 3–60°.

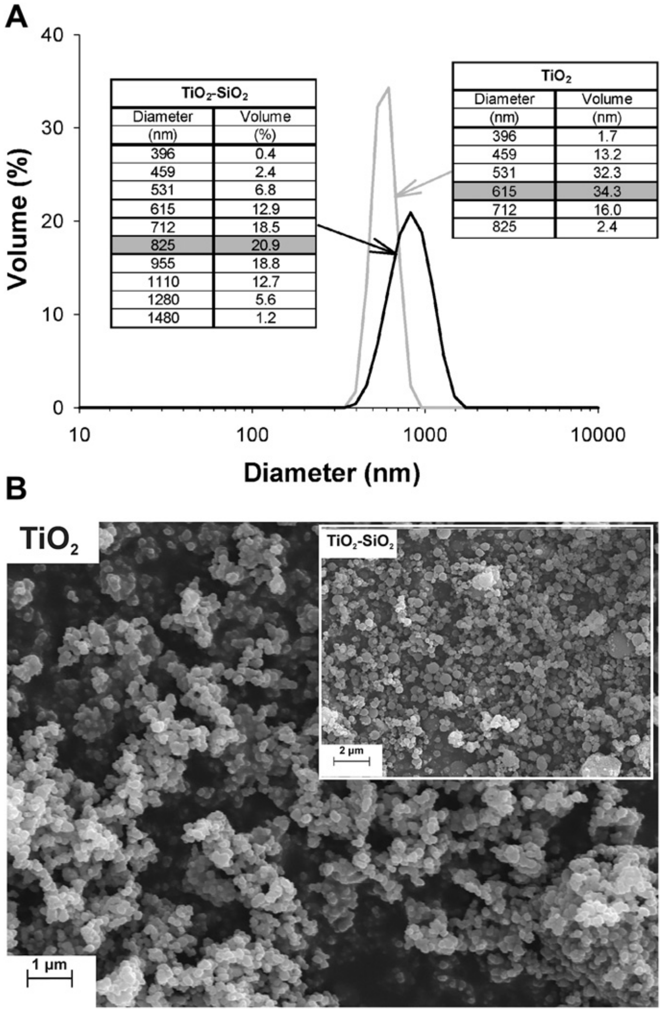
The chemical composition of TiO_2 and TiO_2–SiO_2 and randomly selected hybrid pigments was carried out using a Vario EL Cube apparatus (Elementar).

The effectiveness of the dye adsorption process was also evaluated on the basis of zeta potential measurements. Using a Zetasizer Nano ZS equipped with an autotitrator (Malvern Instruments Ltd.) it was also possible to measure electrophoretic mobility and indirectly the zeta potential, using laser Doppler velocimetry (LDV). The electrokinetic potential was measured in the presence of a 0.001 M NaCl electrolyte over the whole considered pH range, which enabled determination of the electrokinetic curves. To perform the measurements 0.01 g of a sample was dispersed in 25 cm^3 of NaCl electrolyte. Then 10 cm^3 of the sample so prepared was placed in a titrator enabling automatic titration of the system either with an acid (0.2 M HCl) or with a base (0.2 M NaOH). The measurements gave the dependence of the zeta potential on pH. For each sample, twelve measurements were made, the accuracies of the measurements being ±0.01 mV (zeta potential) and ±0.01 (pH).

3. Results

3.1. Physicochemical characterisation of inorganic supports based on TiO_2

The aim of the first stage of the study was to characterise the morphology and dispersive properties of the inorganic supports based on commercial TiO_2 and synthetic TiO_2–SiO_2 oxide composite. The particle size distribution according to the volume contribution obtained for KRONOS 1171 is presented in Fig. 1A, and



TiO_2-SiO_2	
Diameter (nm)	Volume (%)
396	0.4
459	2.4
531	6.8
615	12.9
712	18.5
825	20.9
955	18.8
1110	12.7
1280	5.6
1480	1.2

TiO_2	
Diameter (nm)	Volume (nm)
396	1.7
459	13.2
531	32.3
615	34.3
712	16.0
825	2.4

Fig. 1. Particle size distributions by volume (A) and SEM microphotographs (B) of inorganic supports based on TiO_2.

shows one relatively narrow band covering particle diameters from 396 to 825 nm; the maximum volume contribution of 34.3% comes from particles of 615 nm diameter. The polydispersity index of this pigment is 0.133, which means that this sample is rather homogeneous. The particle size distribution of TiO_2–SiO_2 oxide composite shows one broad band, corresponding to particles and primary agglomerates with diameters ranging from 396 to 1480 nm (the maximum volume contribution of 20.9% corresponds to agglomerates of 825 nm diameter). The polydispersity index of this pigment is 0.206.

The results presented prove that the inorganic supports studied are made of particles of almost spherical shape and with a considerable tendency to agglomerate. The SEM microphotographs of the samples studied presented in Fig. 1B confirm the presence of particles of small diameter (corresponding to those indicated in the particle size distributions), with high homogeneity. Moreover, the synthetic oxide composite sample contains particles of higher diameters than those in the commercial TiO_2.

The adsorptive properties of TiO_2 and TiO_2–SiO_2 oxide composite were characterised by determining the nitrogen adsorption/desorption isotherms and calculating the surface area, mean size and total volume of pores. The isotherms recorded for TiO_2 pigment and TiO_2–SiO_2 oxide composite indicated the mesoporous character of the samples; see Fig. 2A. The highest surface area (A_{BET}), 188.7 m^2/g, was found for TiO_2–SiO_2 oxide composite. The hysteresis loop of TiO_2–SiO_2 covers the relative pressure range $p/p_0 = 0.4$–1.0. The mean pore diameter of this substance is 2.9 nm and the total pore volume is 0.14 cm^3/g. For this sample the amount of nitrogen adsorbed for relative pressure in the range $p/p_0 = 0$–0.8 slowly increases; above $p/p_0 = 0.8$ the amount of nitrogen adsorbed rapidly increases to reach a maximum value of 132 cm^3/g at $p/p_0 = 1.0$. For TiO_2 pigment, the nitrogen volume adsorbed at $p/p_0 = 1.0$ is much lower (22 cm^3/g), its mean pore diameter is 40.1 nm, and the total pore volume is 0.02 cm^3/g. The commercial TiO_2 shows low surface activity; its specific surface area is 2.1 m^2/g. Adsorptive parameters, especially the surface activity of inorganic oxide systems, significantly influence the adsorption of selected organic compounds.

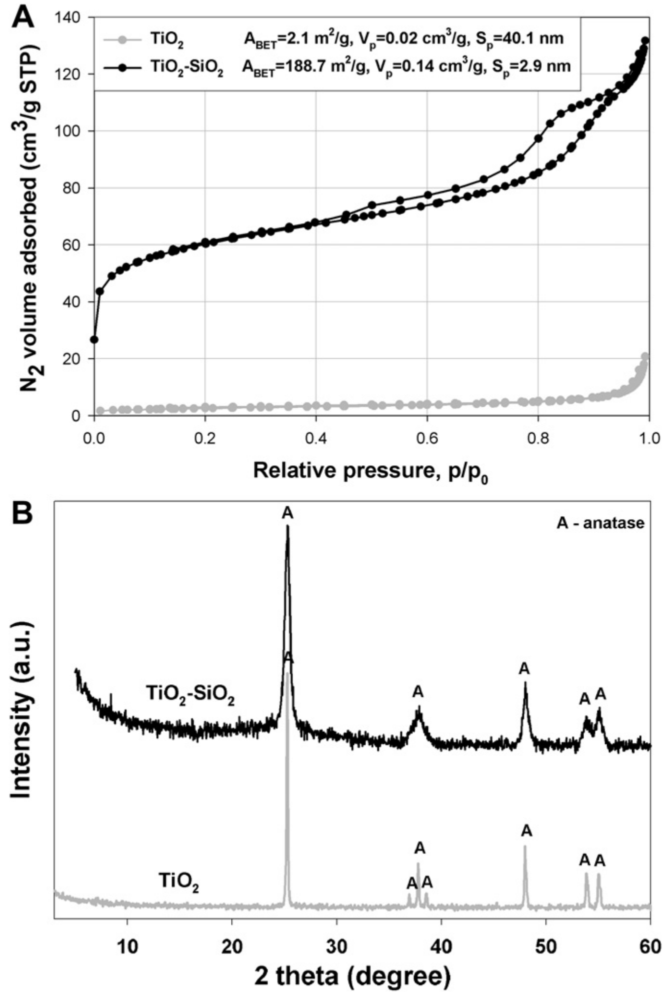


Fig. 2. N_2 adsorption/desorption isotherms (A) and WAXS patterns (B) of inorganic supports TiO_2 and TiO_2–SiO_2.

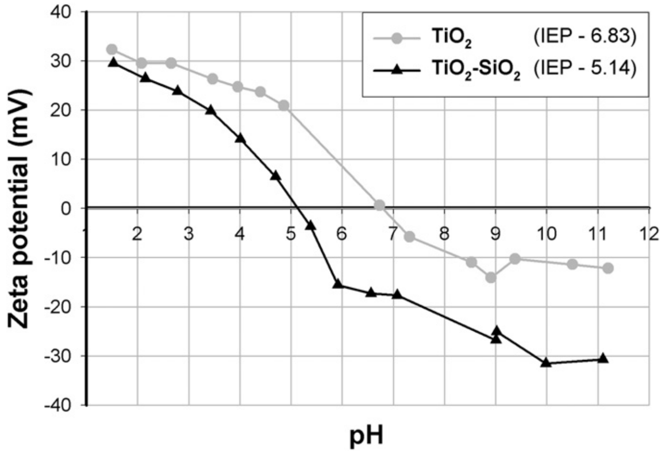


Fig. 3. Electrokinetic curves of the TiO_2 and TiO_2–SiO_2 supports examined.

The structures of inorganic supports based on titanium dioxide were studied using the WAXS method. Titania of well-defined crystalline structure shows maxima in the WAXS patterns at certain specific 2 theta values. The anatase structure is characterised by the presence of maxima at 2Θ values of 25, 32, 33, 33.5, 48, 54 and 55 [24]. Fig. 2B shows the WAXS patterns of TiO_2 and TiO_2–SiO_2 oxide composite samples with an anatase structure.

Following the preliminary characterisation described above, the samples of titanium dioxide and TiO_2–SiO_2 oxide composite were subjected to electrokinetic tests. The zeta potential provides information on changes in the surface properties and stability of dispersion.

The curves of zeta potential versus pH, determined for the commercial titanium dioxide and TiO_2–SiO_2 oxide composite supports, are shown in Fig. 3. The IEP of commercial TiO_2 occurs at pH 6.83; its maximum zeta potential is 32.3 mV, and the minimum −12.2 mV. The IEP of TiO_2–SiO_2 oxide composite is

Table 2
Adsorption efficiency (W) and degree of dye elution (X) for selected food dyes supported on TiO_2.

Initial dye concentration (mg/dm^3)	TiO_2					
	C.I. Food Yellow 4		C.I. Food Blue 5:2		C.I. Food Red 9	
	W (%)	X (%)	W (%)	X (%)	W (%)	X (%)
10	37.0	0.8	7.0	1.0	10.0	12.0
15	44.0	6.2	25.3	0.3	14.0	28.6
20	31.0	7.9	11.0	0.8	13.5	14.8
25	36.0	4.4	12.8	0.9	10.8	4.8
30	40.7	1.8	10.7	1.7	17.3	2.3
35	30.6	2.0	14.9	1.0	23.4	1.2
40	47.0	1.2	16.0	0.9	24.3	4.3
45	42.2	2.0	17.1	1.4	26.9	3.3
50	44.8	1.7	18.4	0.9	28.2	5.7

Table 3
Adsorption efficiency (W) and degree of dye elution (X) for selected food dyes supported on TiO_2–SiO_2 oxide composite.

Initial dye concentration (mg/dm^3)	TiO_2–SiO_2					
	C.I. Food Yellow 4		C.I. Food Blue 5:2		C.I. Food Red 9	
	W (%)	X (%)	W (%)	X (%)	W (%)	X (%)
10	29.8	59.3	99.2	25.3	71.6	32.7
15	29.7	62.9	60.6	26.3	62.1	19.8
20	34.4	34.8	90.4	37.6	62.1	22.3
25	36.0	37.4	88.3	33.5	60.0	20.0
30	44.5	32.0	82.0	35.4	62.7	14.4
35	44.2	34.0	87.7	37.4	59.6	26.4
40	37.0	38.0	81.5	40.0	50.7	40.2
45	39.0	41.8	79.1	41.3	53.2	33.3
50	33.0	40.0	77.0	40.0	47.9	30.0

shifted towards a lower pH (5.14). The maximum zeta potential is 29.5 mV at pH 1.53, and its minimum −31.6 mV at pH 9.98.

3.2. Adsorption efficiency and stability of the hybrid pigments

The next stage of the study involved establishing the efficiency of food dye adsorption on the surface of inorganic supports and the stability of pigments obtained. This was done by taking measurements of the absorbance of the post-process solutions (Tables 2 and 3).

Table 2 presents the adsorption efficiencies and degrees of selected food dyes' elution from the commercial TiO_2 support. Adsorption of the dyes was performed on inorganic pigment in a wide range of dye concentrations, from 10 to 50 mg/dm^3. As follows from the above results, C.I. Food Yellow 4 is the strongest adsorbed on the surface of commercial TiO_2; the efficiency of its adsorption varies between 30.6 and 47.0%. Its highest value (47.0%) is achieved for the pigment obtained from a dye concentration of 40 mg/dm^3 in the initial solution. The results describing the stability of the hybrid pigments, obtained in the dye elution tests, did not suggest any correlation between the dye solution concentration and pigment stability. The degree of dye elution from the TiO_2 surface was random. It was highest (7.9%) for the sample obtained after adsorption of C.I. Food Yellow 4 with a concentration of 20 mg/dm^3 in the initial solution.

The efficiency of adsorption of C.I. Food Blue 5:2 was much lower; it varied from 7.0 to 25.3%. The degree of dye elution from the support was very low, and was lowest – at just 1.7% – for the sample obtained after adsorption of dye in a concentration of 30 mg/dm^3.

For the pigments made of TiO_2 support and C.I. Food Red 9, with increasing dye concentration in the initial solution the efficiency of adsorption increased up to 28.2% for a concentration in initial solution of 50 mg/dm^3. The degree of dye elution from TiO_2 surface was mostly random and for some samples was close to 30.0%. Also the degree of elution of C.I. Food Red 9 from TiO_2 decreased with its increasing concentration in the initial solution used for adsorption.

The pigments obtained after adsorption of C.I. Food Blue 5:2 were much more stable. In conclusion, the yellow dye was found to be more effectively adsorbed on the surface of TiO_2 and the hybrid pigments obtained with this dye were rather stable. The efficiency of adsorption of the blue food dye was low, irrespective of the dye concentration in the initial solution.

At the next step, the adsorption efficiency of three selected food dyes (C.I. Food Yellow 4, C.I. Food Blue 5:2 and C.I. Food Red 9) on the surface of TiO_2–SiO_2 synthetic inorganic support of anatase form was examined.

Table 3 presents the adsorption efficiencies of the selected dyes and degrees of their elution from the hybrid pigment surface. The highest efficiency of adsorption, 99.2%, was obtained for the pigment made of C.I. Food Blue 5:2 in the lowest concentration in the initial dye solution, 10 mg/dm^3. For the pigments obtained by adsorption of C.I. Food Red 9 the efficiencies of adsorption were in the range 50.7–71.6%. By far the lowest were the efficiencies of adsorption of C.I. Food Yellow 4; their values ranged from 29.7 to 44.5%. For the samples obtained after adsorption of C.I. Food Blue 5:2 and C.I. Food Red 9, the efficiency of dye adsorption decreases with increasing dye concentration in the initial solution, e.g. the efficiency was 77.0% for the sample obtained using C.I. Food Blue 5:2 with a concentration of 50 mg/dm^3 in the initial solution. Also for the samples obtained after adsorption of C.I. Food Red 9 the lowest efficiency of 47.9% was recorded when the initial dye solution concentration was 50 mg/dm^3. For the red dye similar changes were observed. The stability of the hybrid pigments was assessed based on the elution tests. In general, the degree of elution was very high, and the highest value, about 40.0%, was achieved for the pigments obtained after adsorption of the dyes from the initial solution of the highest concentration. The lowest degrees of elution, 25.3 and 14.4%, were recorded for pigments obtained after adsorption of C.I. Food Blue 5:2 and C.I. Food Red 9 from initial solution concentrations of 10 and 30 mg/dm^3 respectively.

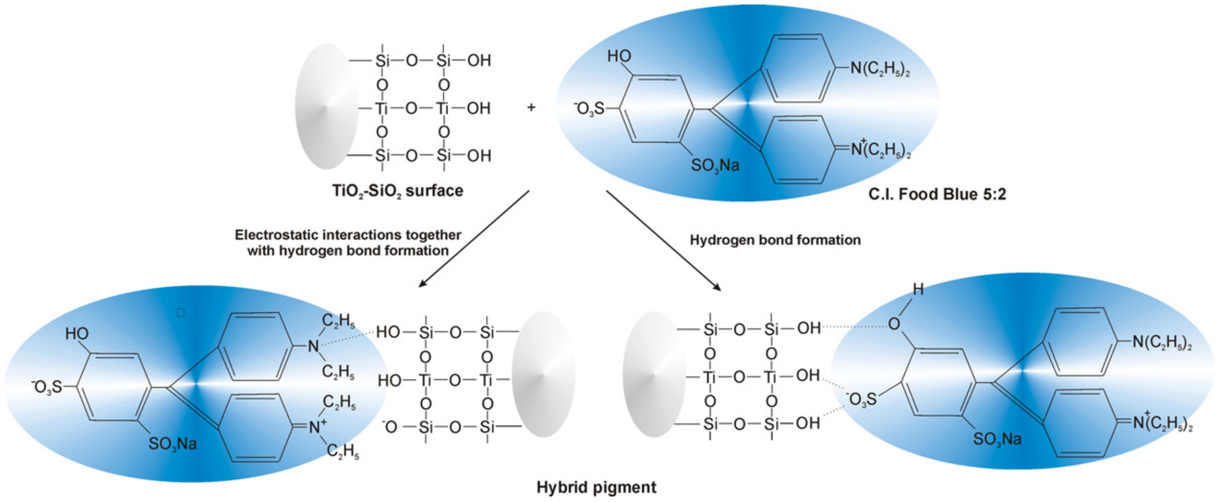


Fig. 4. Mechanism of C.I. Food Blue 5:2 adsorption on TiO_2–SiO_2 surface.

As follows from the above results, the food dyes are more strongly adsorbed on the surface of synthetic TiO_2–SiO_2 oxide composite. Moreover, the degree of the dyes' elution from the surface of TiO_2–SiO_2 oxide composite is significantly higher than that from TiO_2 pigments, which means that they are less stable.

The proposed mechanism of blue dye (C.I. Food Blue 5:2) adsorption on inorganic TiO_2-SiO_2 support is presented in Fig. 4.

3.3. Dispersive and morphological properties of the hybrid pigments

The morphological and dispersive properties of titanium dioxide and TiO_2–SiO_2 oxide composite with selected adsorbed food dyes were determined. The main aim of the study was to evaluate the efficiency of the adsorption process for commercial

Table 4
Dispersive and morphological properties of hybrid pigments obtained using TiO_2.

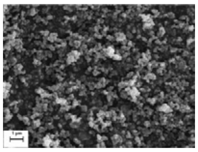
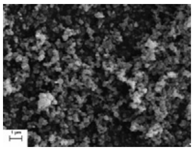
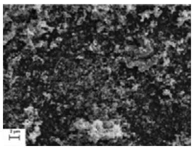
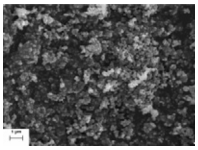
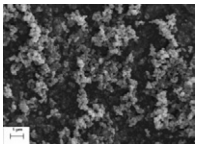
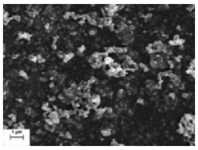
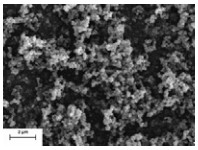
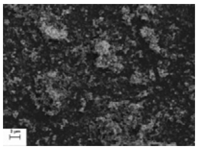
Initial dye concentration (mg/dm^3)	TiO_2		
	Particle size distributions by volume (nm) and maximum volume contribution (%)	Polydispersity index	SEM microphotographs
	C.I. Food Yellow 4		
10	396–1720 (712 nm–20.3)	0.184	
30	396–1110 (712 nm–32.9)	0.220	
50	459–1990 (825 nm–19.7)	0.108	
	C.I. Food Blue 5:2		
10	615–2300 (1280 nm–21.7)	0.161	
30	615–2670 (1280 nm–20.9)	0.187	
50	615–2300 (1110 nm–20.3)	0.162	
	C.I. Food Red 9		
10	342–955 (531 nm–25.5)	0.089	–
30	342–712 (531 nm–35.8)	0.294	
50	712–1990 (1110 nm–26.4)	0.331	

Table 5
Dispersive and morphological properties of hybrid pigments obtained using TiO_2–SiO_2 oxide composite.

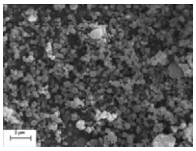
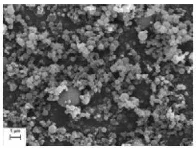
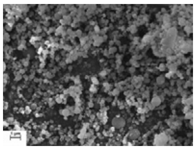
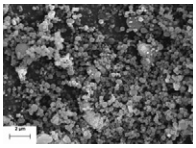
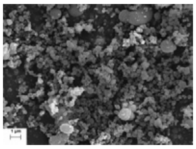
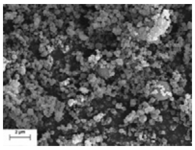
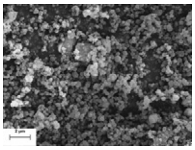
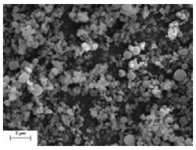
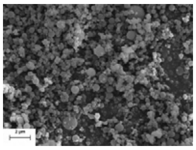
Initial dye concentration (mg/dm^3)	TiO_2–SiO_2		
	Particle size distributions by volume (nm) and maximum volume contribution (%)	Polydispersity index	SEM microphotographs
	C.I. Food Yellow 4		
10	342–1280 (712 nm–19.1)	0.097	
30	342–1480 (712 nm–21.6)	0.072	
50	342–825 (531 nm–29.1)	0.129	
	C.I. Food Blue 5:2		
10	396–1480 (825 nm–20.9)	0.267	
30	342–1480 (712 nm–21.6)	0.161	
50	342–1110 (615 nm–23.7)	0.134	
	C.I. Food Red 9		
10	295–1280 (615 nm–21.5)	0.209	
30	342–955 (531 nm–27.9)	0.297	
50	295–955 (531 nm–25.5)	0.204	

Table 6
Adsorptive properties of TiO_2-based hybrid pigments.

Initial dye concentration (mg/dm^3)	TiO_2								
	C.I. Food Yellow 4			C.I. Food Blue 5:2			C.I. Food Red 9		
	A_{BET} (m^2/g)	V_p (cm^3/g)	S_p (nm)	A_{BET} (m^2/g)	V_p (cm^3/g)	S_p (nm)	A_{BET} (m^2/g)	V_p (cm^3/g)	S_p (nm)
10	5.3	0.004	3.1	6.3	0.005	3.0	6.1	0.005	3.0
20	6.6	0.004	2.8	5.8	0.004	3.0	6.1	0.005	3.0
30	5.5	0.004	3.2	5.6	0.004	3.1	5.9	0.005	3.1
40	5.7	0.005	3.2	6.8	0.004	2.6	8.8	0.003	1.6
50	6.2	0.005	3.0	6.4	0.005	3.0	7.6	0.004	2.2

titanium dioxide as well as TiO_2–SiO_2 oxide composite, and to determine the effect of this process on the principal physicochemical properties of the systems obtained. Tables 4 and 5 give the dispersive and morphological properties of the TiO_2 and TiO_2–SiO_2 based pigments.

Notable differences in the mean particle diameters of hybrid pigments obtained after adsorption of selected food dyes on TiO_2 were observed, which were manifested in the dispersive properties of the final products. As follows from Table 4, significant changes in the particle size of the hybrid pigments depend on the type and structure of the food dye used. The best dispersive properties were observed for hybrid pigments obtained using C.I. Food Red 9. In general, the hybrid pigments obtained after adsorption of selected food dyes on TiO_2–SiO_2 oxide composite have particles of smaller diameter than in those prepared using the commercial titanium dioxide (see Table 5). There was not observed any significant influence of TiO_2–SiO_2 surface coverage with selected food dyes on the dispersive properties of the hybrid systems obtained.

3.4. Adsorptive properties of the hybrid pigments

The adsorptive properties of titanium dioxide and TiO_2–SiO_2 based hybrid pigments were characterised. The fundamental parameters determining the surface activity of the samples obtained, surface area (A_{BET}) and pore size distribution, are given in Tables 6 and 7. Adsorption of the studied food dyes on the surface of titanium dioxide and TiO_2–SiO_2 caused significant changes in the adsorption parameters of the hybrid pigments. Analysis of the data presented in Table 6 shows that the surface area (A_{BET}) of the pigments increases with increasing concentration of the dye in the solution used for adsorption. A considerable increase in the surface area value of the pigments based on TiO_2–SiO_2 relative to that of the commercial TiO_2 was observed. After adsorption of C.I. Food Yellow 4 on TiO_2 support, the highest surface area (relative to that of the E171 sample) was noted for the sample obtained using a dye concentration of 20 mg/dm^3 in the initial solution. For this sample the surface area was 6.6 m^2/g, the mean pore diameter 2.8 nm and the total pore volume 0.004 cm^3/g. The nitrogen adsorption/desorption isotherms for E171, with C.I. Food Blue 5:2 adsorbed, confirm that the highest surface area of 6.8 m^2/g was observed for the sample prepared using an initial dye solution concentration of 40 mg/dm^3. Similarly as for C.I. Food Yellow 4, all samples with blue dye adsorbed revealed a decrease in the mean pore diameter and pore volume. Among the samples obtained after adsorption of C.I. Food Red 9, the highest surface area of 8.8 m^2/g (relative to that of E171) was found for that obtained with initial dye solution concentration 40 mg/dm^3. The mean pore diameter and pore volume of the red pigments decreased relative to those for the reference sample E171.

As follows from the adsorption analysis of the pigments obtained after adsorption of food dyes on TiO_2, with increasing concentration of the dye in the adsorbate solution the surface area increases. This fact is most probably related to the appearance of new active centres on the titania surface, which enhance its activity.

Table 7 presents the basic parameters describing the adsorptive properties of hybrid pigments obtained after adsorption of selected food dyes on TiO_2–SiO_2. Their analysis suggests that changes in the adsorption parameters for these samples are absolutely random. Adsorption of C.I. Food Yellow 4, C.I. Food Blue 5:2 and C.I. Food Red 9 on TiO_2–SiO_2 results in a reduction in the surface area A_{BET} relative to that of pure TiO_2–SiO_2. The specific surface area of TiO_2–SiO_2 is 188.7 m^2/g, while its pore volume is 0.14 cm^3/g and the mean pore diameter is 2.9 nm. The surface area of the hybrid pigments obtained after adsorption of C.I. Food Yellow 4 varies in the range 121.0–131.0 m^2/g, those obtained after adsorption of C.I. Food Blue 5:2 give values in the range 116.5–135.3 m^2/g, and those obtained after adsorption of C.I. Food Red 9 give values in the range 97.0–137.6 m^2/g. These significant changes in the surface activity are most probably related to the blocking of active centres by the dye molecules. As to the total pore volume, the lowest values of this parameter were observed for the hybrid pigments obtained after adsorption of C.I. Food Red 9 from solutions of different concentrations (0.076–0.106 cm^3/g). No significant changes in the mean pore diameter were noted between the oxide support and the hybrid pigments.

The results describing the adsorptive properties of the pigments based on TiO_2–SiO_2 are directly correlated to those concerning the adsorption efficiency of the food dyes used, which confirms the change in the surface activity of the pigments as well as the effectiveness of the adsorption process.

Table 7
Adsorptive properties of TiO_2–SiO_2-based hybrid pigments.

Initial dye concentration (mg/dm^3)	TiO_2–SiO_2								
	C.I. Food Yellow 4			C.I. Food Blue 5:2			C.I. Food Red 9		
	A_{BET} (m^2/g)	V_p (cm^3/g)	S_p (nm)	A_{BET} (m^2/g)	V_p (cm^3/g)	S_p (nm)	A_{BET} (m^2/g)	V_p (cm^3/g)	S_p (nm)
10	121.0	0.093	3.1	135.3	0.105	3.1	137.6	0.106	3.1
20	124.5	0.096	3.1	132.2	0.101	3.1	108.6	0.083	3.1
30	131.0	0.100	3.1	116.5	0.090	3.1	109.6	0.085	3.1
40	130.0	0.101	3.1	132.2	0.102	3.1	97.0	0.076	3.1
50	129.3	0.099	3.1	135.3	0.104	3.1	121.0	0.094	3.1

Table 8
The degree of coverage of TiO_2 surface with food dyes adsorbed from solutions of different concentrations.

Initial dye concentration (mg/dm^3)	TiO_2											
	C.I. Food Yellow 4				C.I. Food Blue 5:2				C.I. Food Red 9			
	Elemental content (%)			P* (μmol/m^2)	Elemental content (%)			P* (μmol/m^2)	Elemental content (%)			P* (μmol/m^2)
	C	H	S		C	H	S		C	H	S	
10	0.061	0.014	0.024	1.281	0.063	0.016	0.021	0.922	0.093	0.017	0.030	1.859
20	0.048	0.014	0.022	1.007	0.053	0.014	0.025	0.782	0.090	0.015	0.031	1.792
30	0.061	0.014	0.022	1.274	0.052	0.014	0.019	0.768	0.067	0.014	0.026	1.331
40	0.066	0.018	0.031	1.377	0.066	0.015	0.024	0.976	0.063	0.014	0.023	1.244
50	0.078	0.017	0.027	1.632	0.057	0.015	0.022	0.832	0.072	0.015	0.023	1.423

P* - coverage degree of dye.

3.5. The degree of coverage of inorganic supports with selected food dyes

To confirm the effectiveness of adsorption of selected food dyes on the surface of TiO_2 or TiO_2–SiO_2, the percentage content of elements characteristic of a given dye, and the degree of the substrate surface coverage, were determined. The degree of coverage was evaluated on the basis of the Berendsen and de Golan equation [25]. Tables 8 and 9 present the calculated degree of coverage of inorganic supports based on titanium dioxide with food dyes, for different dye concentrations in the initial solution used for the pigments production. As follows from the elemental analysis, the percentage contents of such elements as carbon or sulphur in the pigments obtained after adsorption of C.I. Food Yellow 4, C.I. Food Blue 5:2 or C.I. Food Red 9, from solutions of different concentrations, show random changes. Most probably changes of this type were due to the fact that the adsorbate solutions were of relatively low concentrations, which is related to the future applications of the pigments.

The elemental analysis proved that the percentage content of carbon in the pigments obtained after adsorption of C.I. Food Yellow 4, C.I. Food Blue 5:2 or C.I. Food Red 9 from solutions of different concentrations show random changes (see Table 8). Higher percentage carbon content values were recorded for the pigments obtained after adsorption of C.I. Food Red 9, and the highest (0.093%) was found for the pigment obtained after adsorption of this dye from an initial solution concentration of 10 mg/dm^3. The lowest percentage content of carbon was noted for the pigments obtained after adsorption of C.I. Food Blue 5:2. The hybrid pigments obtained after adsorption of this dye are also characterised by the lowest degree of surface coverage, in the range 0.078–0.976 μmol/m^2. The highest degree of TiO_2 surface coverage, in the range 1.244–1.859 μmol/m^2, was found for the pigments obtained using C.I. Food Red 9.

The effectiveness of adsorption of selected food dyes can be evaluated from the increase in the percentage content of carbon and sulphur in the pigments, relative to their content in the TiO_2–SiO_2 sample (see Table 9). The highest percentage content values for carbon and sulphur were recorded for the pigments obtained after adsorption of C.I. Food Blue 5:2, which correlates with the established adsorption efficiencies. The highest percentage content of carbon (0.175%) was found for the pigment obtained after adsorption of this dye from a solution concentration of 50 mg/dm^3, while the highest percentage content of sulphur was detected for the pigment obtained after adsorption of C.I. Food Blue 5:2 from an initial solution with concentration 40 mg/dm^3. The highest degree of TiO_2–SiO_2 surface coverage, in the range 0.026–0.039 μmol/m^2, was noted for the pigment obtained using C.I. Food Red 9. This result is in contrast to the low percentage content of carbon and sulphur, which follows from the fact that for calculation of the degree of coverage the molecular weight of a given dye is taken into account, and the molecular weight of this red dye was much different from those of the other dyes used. Similarly as the changes in the percentage content of carbon and sulphur, the changes in the degree of coverage also cannot be correlated to the initial dye solution concentrations and are random in character.

As follows from the above results, the adsorption of food dyes from initial dye solutions with concentrations up to 50 mg/dm^3, on the surface of inorganic supports, is an effective process and produces pigments with specific physicochemical properties.

3.6. Electrokinetic properties of hybrid pigments obtained after adsorption of food dyes on inorganic supports based on TiO_2

The efficiency of surface coverage of inorganic oxides with selected dyes can be readily estimated from the electrokinetic behaviour, i.e. measurements of zeta potential. Thus, in the next step, samples of titanium dioxide and TiO_2–SiO_2 oxide composite with adsorbed selected food dyes were subjected to tests of their electrokinetic properties. Fig. 5 presents the zeta potential vs. pH dependencies evaluated for the hybrid pigments prepared using titanium dioxide or TiO_2–SiO_2.

Table 9
The degree of coverage of TiO_2–SiO_2 oxide composite surface with food dyes adsorbed from solutions of different concentrations.

Initial dye concentration (mg/dm^3)	TiO_2–SiO_2											
	C.I. Food Yellow 4				C.I. Food Blue 5:2				C.I. Food Red 9			
	Elemental content (%)			P* (μmol/m^2)	Elemental content (%)			P* (μmol/m^2)	Elemental content (%)			P* (μmol/m^2)
	C	H	S		C	H	S		C	H	S	
10	0.107	0.816	0.051	0.023	0.119	0.906	0.056	0.020	0.118	0.890	0.054	0.026
20	0.105	0.832	0.050	0.024	0.103	0.906	0.054	0.017	0.127	0.885	0.055	0.028
30	0.109	0.840	0.055	0.025	0.137	0.896	0.063	0.022	0.174	0.874	0.069	0.039
40	0.105	0.840	0.055	0.024	0.163	0.884	0.071	0.027	0.129	0.803	0.055	0.029
50	0.118	0.837	0.056	0.028	0.175	0.887	0.065	0.029	0.134	0.793	0.051	0.030

P* - coverage degree of dye.

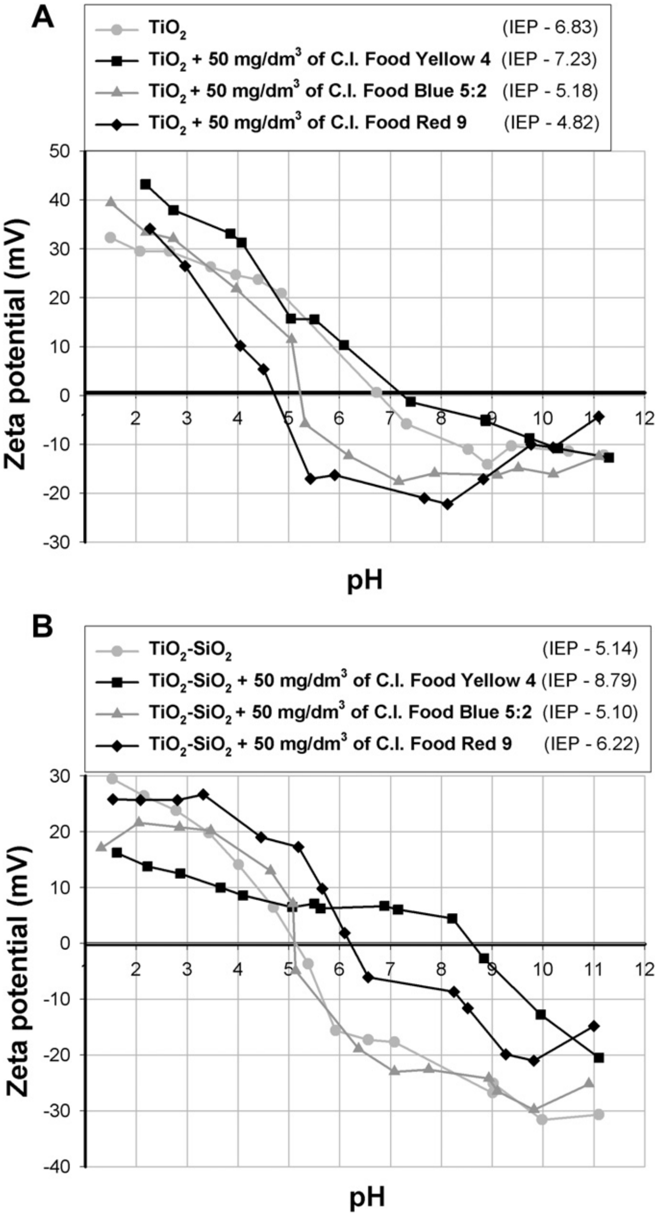


Fig. 5. Zeta potential vs. pH of hybrid pigments obtained after adsorption of different food dyes on (A) TiO_2 and (B) $TiO_2–SiO_2$ oxide composite.

Fig. 5 presents the electrokinetic curves examined for the pigments obtained with selected food dyes (C.I. Food Yellow 4, C.I. Food Blue 5:2 and C.I. Food Red 9 concentration of 50 mg/dm^3 in the initial solutions) and inorganic supports based on titanium dioxide. Adsorption of food dyes on the surface of TiO_2 resulted in significant changes in the character of the electrokinetic curves. The electrokinetic curves for the hybrid pigments based on C.I. Food Blue 5:2 and C.I. Food Red 9 are slightly shifted towards lower pH, relative to the curve for pure TiO_2. After adsorption of the two above-mentioned food dyes on commercial TiO_2, the isoelectric points of the hybrid pigments obtained were 5.18 and 4.82 respectively. The electrokinetic curve for the hybrid pigment obtained using C.I. Food Yellow 4 (concentration of 50 mg/dm^3 in the initial solution) has a similar character as that of the curve recorded for pure TiO_2. The IEP value of this hybrid pigment occurs at pH 7.23.

In the next stage of the study, zeta potential was measured for TiO_2-SiO_2 oxide composite with selected food dyes adsorbed from the initial solution with concentration 50 mg/dm^3 Fig. 5B presents the electrokinetic curves for the hybrid pigments after adsorption of C.I. Food Yellow 4, C.I. Food Blue 5:2 and C.I. Food Red 9. The IEP of $TiO_2–SiO_2$ oxide composite is at 5.14. Adsorption of food dyes on the synthetic oxide composite caused different significant changes in its electrokinetic properties. The electrokinetic curve for the pigment obtained after C.I. Food Blue 5:2 adsorption from the initial solution of concentration 50 mg/dm^3 was the same as for pure $TiO_2–SiO_2$. The IEP values were also very similar – 5.14 for $TiO_2–SiO_2$ oxide composite and 5.10 for this pigment sample. Changes in the electrokinetic properties of the hybrid pigments obtained after adsorption of C.I. Food Yellow 4 and C.I. Food Red 9 are manifested in the electrokinetic curves and IEP shift towards higher pH in comparison with those of the pure $TiO_2–SiO_2$ sample. For these hybrid pigments the IEPs appeared at 8.79 and 6.22 respectively. The electrokinetic properties of the hybrid pigments prepared depend directly on the type of dye and the efficiency of its adsorption.

4. Discussion

Adsorption of dyes on the surface of $TiO_2–SiO_2$ oxide composite is a complex process. Mechanisms of adsorption and adsorbent/adsorbate interactions have been discussed by P.V. Messina and P.C. Schulz [26], who performed the process of dye adsorption on mesoporous $TiO_2–SiO_2$ obtained by hydrolysis of $TiCl_4$ from OT/water/hexane emulsion followed by addition of surfactants. The authors additionally studied silica of mesoporous structure (MCM-41 and MCM-50 type). The adsorbates were two cationic dyes: methylene blue (MB) – C.I. Basic Blue 9, and rhodamine B (RhB) – C.I. Basic Violet 10. The results of their study showed that with increasing size of the molecules of the dye, its adsorption ability on the mesoporous adsorbent decreases. Also important for the process of dye adsorption are differences in the surface area and porosity of the adsorbents. The adsorption abilities of anionic dyes decrease as a result of electrostatic repulsion.

The adsorption behaviour of methyl orange – C.I. Acid Orange 52 on composite xerogels has been investigated by Z. Wu et al. [27]. Mesoporous $TiO_2–SiO_2$ and $TiO_2–SiO_2–Al_2O_3$ xerogels were prepared by hydrolysis of tetraethyl orthosilicate (TEOS), tetrabutyl orthotitanate (TBOT), and $AlCl_3 \cdot 6H_2O$ using HCl as a catalyst and cetyltrimethylammoniumbromide (CTAB) as a templating agent. In acidic solutions, methyl orange is adsorbed by the mesoporous xerogels, but only slightly adsorbed by the microporous xerogels of identical composition, demonstrating a sieve effect. The C.I. Acid Orange 52 adsorption decreases with pH because of the electrostatic interaction between methyl orange and the xerogel surface. It was also shown that the adsorption isotherms are of Langmuir type and that adsorption decreases with increasing temperature. Those authors suggested that C.I. Acid Orange 52 is adsorbed by electrostatic attraction and hydrogen bonds between methyl orange and the xerogel surface.

G.L. Dotto et al. [28] studied adsorption of the food dyes C.I. Acid Blue 9 and C.I. Food Yellow 3 onto chitosan. For both dyes, the adsorption occurred by film and intraparticle diffusion, and an increase in the stirring rate a decrease in the film diffusion resistance. Therefore the film diffusivity increased the adsorption capacity and, consequently, intraparticle diffusivity increased. At all stirring rates, the rate-limiting step was film diffusion. Adsorption of C.I. Acid Blue 9 and C.I. Food Yellow 3 onto chitosan occurred by chemisorption.

Adsorption of a cationic dye (methylene blue – C.I. Basic Blue 9) onto spent activated clay has been reported by Ch.-H. Weng et al. [29]. Parameters affecting the adsorption, including initial dye concentration, pH and temperature, were evaluated. The adsorption of C.I. Basic Blue 9 onto spent activated clay was favoured at high pH and higher temperature. The removal of methylene blue by adsorption on spent activated clay was found to be rapid in the initial period of contact, and then it slowed down with increasing reaction time.

A.S. Özcan et al. [30] studied the adsorption of the two dyes C.I. Acid Red 57 (AR57) and C.I. Acid Blue 294 (AB294), onto acid-activated bentonite in aqueous solution in a batch system as a function of the contact time, pH, and temperature. Acidic pH was favourable for the adsorption of these dyes. The surface charge on the adsorbent and the pH of the solution can significantly influence the capacity of the adsorbent with respect to acid dyes, AR57 and AB294 ions. Having an excess of positive charge on their surfaces, acid-activated bentonite has a greater capacity to adsorb acidic dyes.

The adsorption of C.I. Mordant Red 3 on the surface of silica, both unmodified and modified with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane, was studied by T. Jesionowski et al. [31]. The efficiency of adsorption and the degree of silica coverage with the dye increased with increasing concentration of the dye in the initial solution. This effect is more pronounced when using the modified silica as a support in pigment preparation. The degree of dye elution from the silica surface decreases with increasing concentration of the dye in the initial solution. Modification of the silica surface causes a decrease in the degree of dye elution from the SiO_2 support.

Andrzejewska et al. [3] studied pigments obtained by adsorption of organic dyes on a modified surface of titanium dioxide. Modification of titania with two types of aminosilanes, 3-aminopropyltriethoxysilane (APTES) and *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTS), increased the efficiency of adsorption of C.I. Acid Orange 7 dye on its surface. A higher efficiency of adsorption of C.I. Reactive Blue 19 dye on titanium dioxide was obtained following modification with APTES silane. When titanium white was modified with AEAPTS, the efficiency of adsorption of C.I. Reactive Blue 19 dye slightly decreased.

5. Conclusions

According to the results presented above, the yellow dye (C.I. Food Yellow 4) was found to be more effectively adsorbed on the surface of TiO_2, and the pigments obtained with this dye were rather stable. The efficiency of adsorption of the blue food dye (C.I. Food Blue 5:2) was low, irrespective of the dye concentration in the initial solution. An important fact is that the food dyes are most strongly adsorbed on the surface of synthetic TiO_2–SiO_2 oxide composite. Moreover, the degree of dye elution from the surface of TiO_2–SiO_2 oxide composite is significantly greater than that from TiO_2 pigment.

As follows from the analysis of the dispersive properties, the notable changes in the particle size of the hybrid pigments depend on the type and structure of the food dye. The hybrid pigments obtained after adsorption of selected food dyes on TiO_2–SiO_2 oxide composite were characterised by particles of smaller diameter than those obtained with the commercial titanium dioxide.

The type and concentration of food dye in the adsorbate solution used have a significant influence on the surface activity of the hybrid pigments obtained. The surface area of the pigments based on TiO_2 increased proportionally with increasing concentration of the dye in the adsorbate solution, in contrast to the hybrid pigments obtained after food dye adsorption on TiO_2–SiO_2 oxide composite, whose surface area decreased proportionally to increasing dye concentration.

The electrokinetic properties (zeta potential) are strictly related to the chemical structure of the dye and its concentration in the adsorbate solution used for pigment preparation. As follows from the electrokinetic analysis, the surface coverage of the inorganic supports based on titanium dioxide with food dyes brings about considerable changes in their physicochemical properties.

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