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

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ABSTRACT

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

1. Introduction

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

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

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

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

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

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

2. Experimental

2.1. Methods of obtaining silica support

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

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

2.2. Silica functionalisation

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

2.3. Pigment composites preparation

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

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

2.4. Dye elution from the silica support surface

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

2.5. Physico-chemical evaluations

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

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