

Synthesis of inorganic oxide composites with the use of postgalvanic waste solutions of copper(II) sulfate

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The study was undertaken to obtain an oxide composite (inorganic colourful pigment) in the method based on the use of postgalvanic waste solution of copper(II) sulfate. The conditions of the process of precipitation of synthetic $\text{CuO}\cdot\text{SiO}_2$ were optimised by checking the effect of the concentration and the volume ratio of the reagents and the temperature on the physico-chemical parameters of the final product. The oxide composite obtained in the optimum conditions was characterised by high refinement of particles and large specific surface area BET of 326 m^2/g .

Keywords: oxide composite $\text{CuO}\cdot\text{SiO}_2$, waste solution of copper(II) sulfate, precipitation, particle size distribution, surface area, colorimetric characteristics.

INTRODUCTION

Silicon belongs to common elements that form many diverse compounds. An interesting group of silicon compounds are silicates that can have crystalline structure or amorphous form. They can contain water and are then called hydrated. Recently, the interest in synthetic silicates or their derivatives – oxide composites of the formula $\text{MO}\cdot\text{SiO}_2$ has much increased because of their wide use in many branches of industry, e.g. in ceramic industry, rubber industry, in the production of polymer composites and paints¹⁻⁶. The important property of synthetic silicates is their ability to form more connections than the natural ones. Although synthetic silicates have similar chemical composition to their natural counterparts, it does not mean that they also have similar physico-chemical properties. The wide range of properties of synthetic silicates makes them desirable for many applications. Highly dispersed silicates can be used as white or colourful inorganic pigments in the production of paints, fillers and adsorbents⁷⁻¹⁰.

Electrochemical separation of metals from the solutions of their salts is a branch of applied electrochemistry involving electroplating processes for the production of e.g. coating of copper, nickel, chromium, zinc, tin and cadmium¹¹. The postgalvanic wastes make a relatively small contribution in the total volume of industrial wastes but they belong to those containing compounds hazardous for man, water and soil.

In this paper we propose a method of utilisation of one type of such wastes, i.e. postgalvanic waste solutions of copper(II) sulfate for production of oxide composites of the type $\text{CuO}\cdot\text{SiO}_2$ (colourful pigments) of specific morphological and dispersive properties.

EXPERIMENTAL

The synthetic oxide composite ($\text{CuO}\cdot\text{SiO}_2$) was obtained in the precipitation process. The substrates were a solution of sodium silicate and postgalvanic solution of copper(II) sulfate. The process was realised in a laboratory scale. To the reactor filled with the postgalvanic solution of copper(II) sulfate, a solution of sodium silicate was dosed by a peristaltic pump. The influence of the

concentrations of substrates (5, 7 and 10% solutions), the volume ratio of the reagents (1:1, 1:2, 2:1, 1:3 and 3:1) and temperature (20 ÷ 60°C) on the physico-chemical parameters of the final products, was studied. The oxide composite was separated from the post-reaction mixture by filtration with the use of a vacuum pump. The samples were dried at 105°C and subjected to detailed analyses of physico-chemical properties. The size of particles was determined by the instruments Zetasizer Nano ZS (NIBS method) and Mastersizer 2000 (laser diffraction method) made by Malvern Instruments Ltd. The contributions of colours, saturation and shade of colour were determined in colorimetric analysis based on the CIE $L^*a^*b^*$ colour space system (Spectrophotometer Specbos 4000, JETI Technische Instrumente GmbH). The adsorption properties of the composites, in particular specific surface area BET and pore volume and diameter, were studied by ASAP 2020 made by Micromeritics Instruments Co. The morphology and microstructure of the products precipitated were analysed using an electron scanning microscope made by Zeiss VO40.

RESULTS AND DISCUSSION

At the first stage the effect of concentrations (5, 7 and 10%) of the postgalvanic solution of copper(II) sulfate on the parameters of the copper(II) silicate obtained was studied at the constant 5% concentration of the other substrate, sodium silicate.

The process in which a 5% sodium silicate solution was introduced to a 5% solution of copper(II) sulfate at the volume ratio 1:1, at 20°C, gave the oxide composite $\text{CuO}\cdot\text{SiO}_2$ of satisfactory parameters. The particle size distribution in the range of small diameters (Fig. 1a) shows a single band covering the diameters of 122 ÷ 295 nm. The greatest volume contribution (32.5%) of the particles with diameters from this range comes from the particles of 190 nm in diameter. The polydispersity index, informing on the homogeneity of the sample, is 0.879, which means that the particles of the oxide composite obtained have a tendency to agglomeration.

The increase in the concentration of postgalvanic solution of copper(II) sulfate to 7%, with no changes in the other parameters of precipitation, caused a shift of the

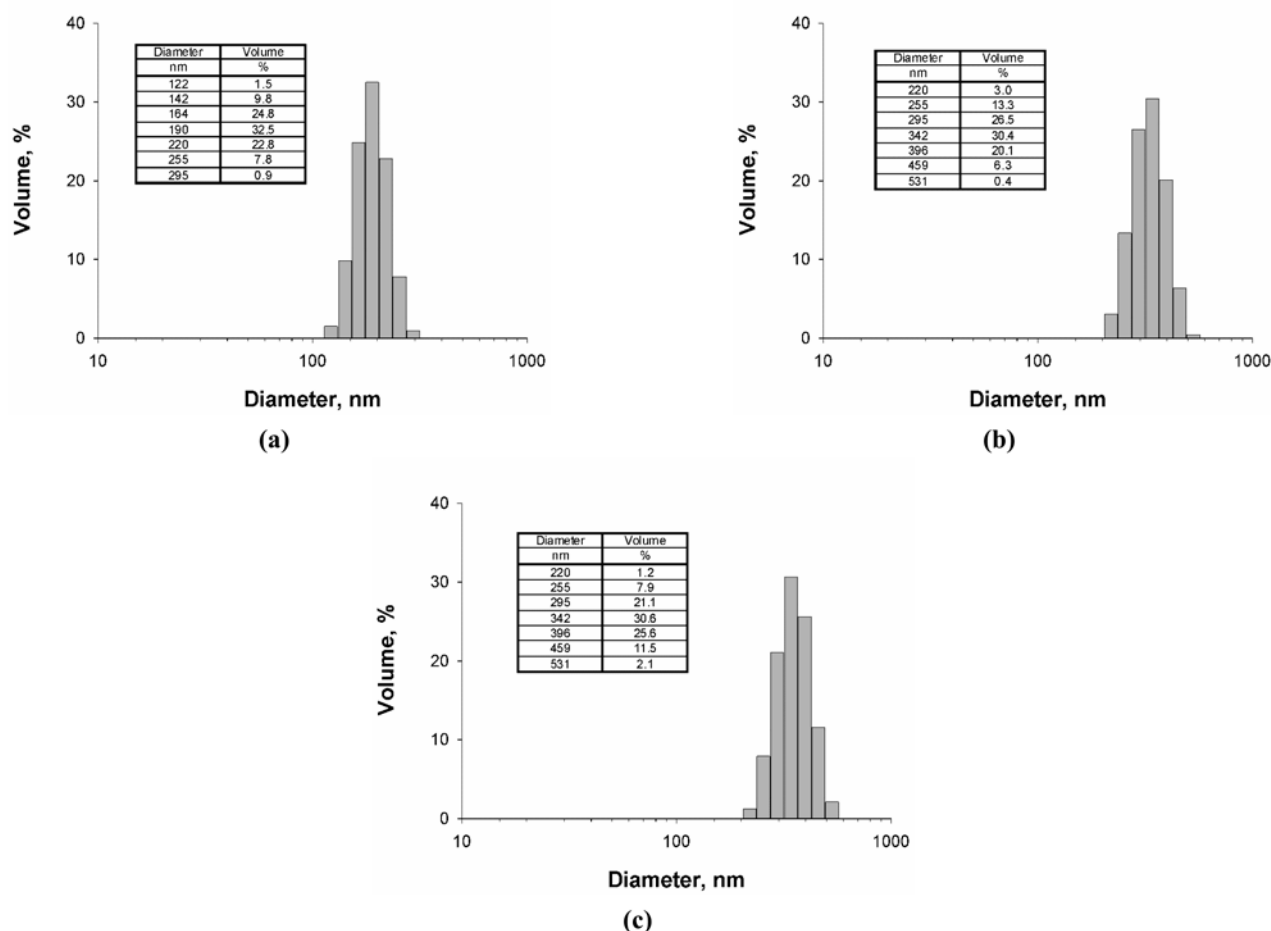


Figure 1. Particle size distributions determined by Zetasizer Nano ZS of the CuO:SiO₂ oxide composites obtained with the use of 5% solution of sodium silicate and (a) 5% (b) 7% or (c) 10% solution of postgalvanic copper(II) sulfate

particle diameters of the oxide composite obtained towards greater values. The particle size distribution for this sample in the range of small diameters (Fig. 1b) showed a single band covering the diameters ranging from 220 to 531 nm. The greatest volume contribution of 30.4% was brought by the particles of 342 nm in diameter. Similar parameters of the oxide composite were obtained when the concentration of the postgalvanic solution was increased to 10%. The particle size distribution for this oxide composite (Fig. 1c) shows also a single band covering the same range of diameters. The greatest volume contribution of 30.6% is brought by the particles of 342 nm in diameter. This change in the concentration of copper(II) sulfate to 7 and 10% also resulted in a decrease in the polydispersity index to 0.266 and 0.189, respectively.

Figure 2 presents the particle size distribution in the range of micrometers (0.2 ÷ 2000 μm) for the oxide composites precipitated using a 5% solution of sodium silicate and 5, 7 and 10% solutions of copper(II) sulfate. When a 5% solution of postgalvanic copper(II) sulfate was used (Fig. 2a), particle distribution measurements revealed the presence of particles of diameters from the range 1.1 ÷ 69.2 μm. The greatest volume contribution of 5.4% was brought by the particles of 15.1 and 17.4 μm in diameter. The sample precipitated with the use of a 7% solution of copper(II) sulfate (Fig. 2b) has particles of diameters from the range 1.3 ÷ 138.0 μm, and the greatest volume contribution of 5.1% is brought by the particles of 30.2 and 34.7 μm in diameter. The sample obtained when using a 10% solution of copper(II) sulfate (Fig. 2c)

has particles of diameters from the range 1.3 ÷ 120.2 μm. The greatest volume contribution of 4.9% is brought by the particles of 8.7, 10.0, 11.5 and 13.2 μm. Fig. 3 presents the SEM images of the oxide composites obtained confirming the presence of particles of diameters in the nano- and micrometric ranges.

SEM photographs (see Fig. 3) for both samples (5% sodium silicate solution and 5 or 7% of the postgalvanic solution of copper(II) sulfate) show either small particles from the diameter range 500 nm or large agglomerate structures (above up to 1000 nm). The observed effect is correlated with the tendency to agglomeration of copper(II) silicate particles obtained in precipitation process. The presence of the agglomerates in the studied samples is also confirmed by the PSD measurements using Mastersizer 2000.

Analysis of the colorimetric data, presented in Fig. 4, has shown that changes in the concentration of copper(II) sulfate exert a definite effect on the brightness of the final samples L^* . The lowest L^* of 67.66 was determined for the sample precipitated from the 7% solution of copper salt, while the highest of 76.47 – for the 10% solution of the salt. The concentration of postgalvanic CuSO₄ also influenced the parameters a^* and b^* . The value of $-a^*$ varied from (-12.75) for 5% CuSO₄ to (-14.63) for 10% CuSO₄, which indicates a considerable contribution of green in the oxide composite colour. The value of $-b^*$ took the lowest value of (-2.60) for the sample obtained with a 10% solution of CuSO₄ and this sample was characterised by the smallest contribution of blue. For the oxide

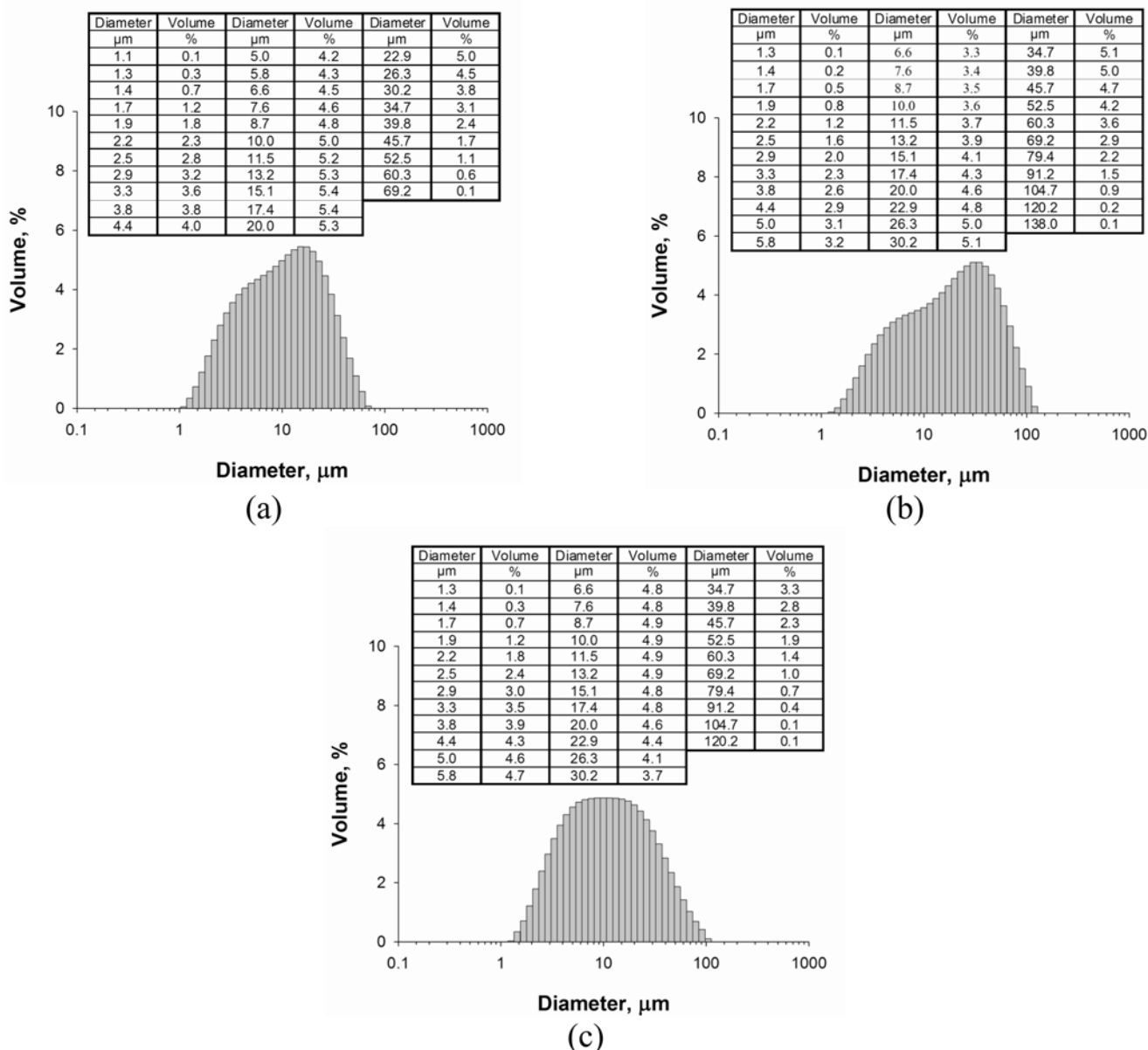


Figure 2. Particle size distributions determined by Mastersizer 2000 of the CuO-SiO₂ oxide composites obtained with the use of 5% solution of sodium silicate and (a) 5% (b) 7% or (c) 10% solution of postgalvanic copper(II) sulfate

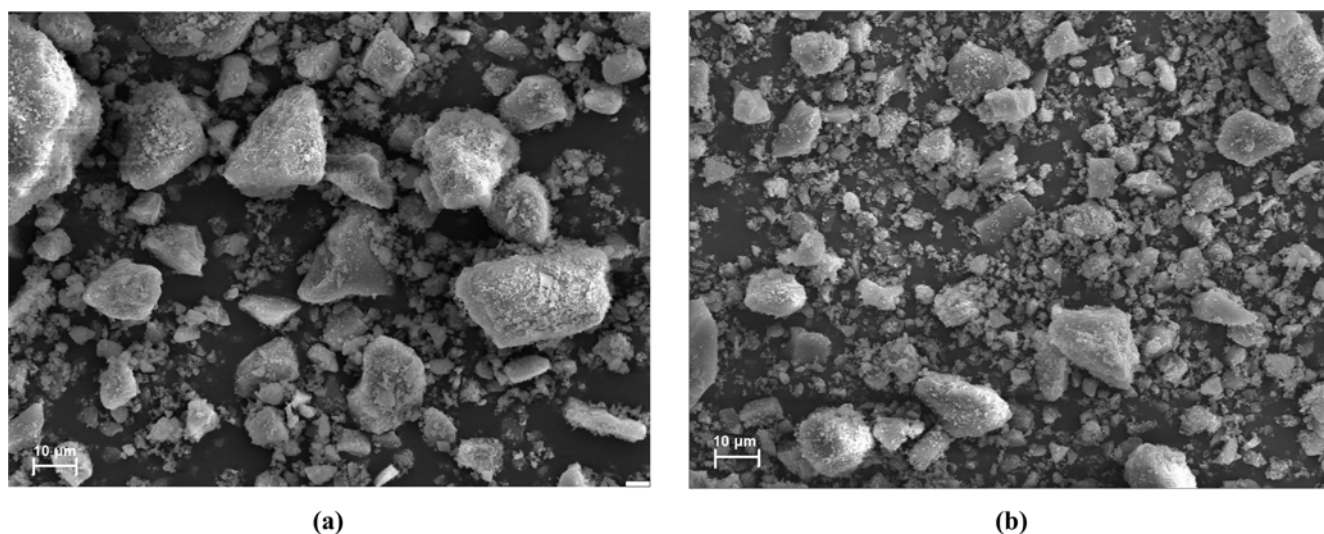


Figure 3. SEM photographs of CuO-SiO₂ composites obtained with the use of 5% solution of sodium silicate and (a) 5% or (b) 7% solution of postgalvanic copper(II) sulfate

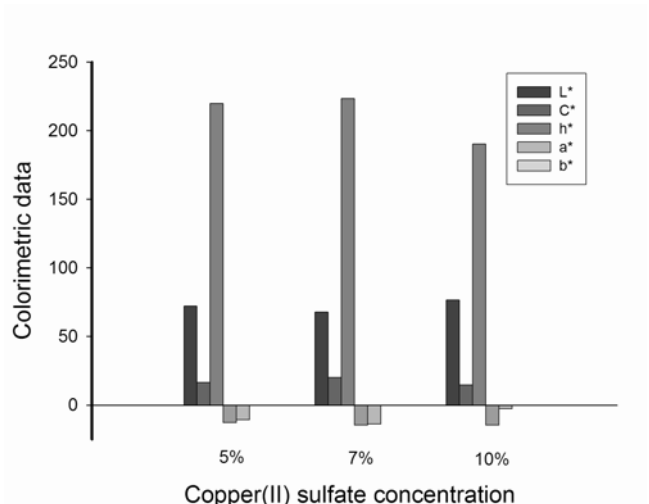


Figure 4. Colorimetric characteristics of CuO-SiO₂ composites obtained with the use of 5% solution of sodium silicate and 5, 7 or 10% solution of postgalvanic copper(II) sulfate

composites obtained with the use of 5 and 7% solutions of CuSO₄, the contribution of blue ($-b^*$) was (-10.58) and (-13.82), respectively.

At the next stage of the study, the influence of the process temperature of precipitation on the particles size of the oxide composite obtained was checked. Fig. 5 presents the particle size distributions in the range of small diameters, for the samples precipitated with the use of 5% solution of sodium silicate and 7% solution of CuSO₄, recorded at two temperatures of 40 and 60°C. As follows from the data, the increased temperature of the process results in increased diameters of the particles of the composites obtained. Moreover, the polydispersity index of the composites increases with temperature (polydispersity of the samples increases) as the values for the samples obtained at 60°C and 20°C are 0.491 and 0.266, respectively.

The particle size distribution in the range of smaller diameters for the sample precipitated at 40°C (Fig. 5a) shows a single band covering the range 295 ÷ 955 nm. The greatest volume contribution of 24.9% is brought by the particles of 531 nm in diameter. For the sample precipitated at 60°C the particle size distribution (Fig. 5b)

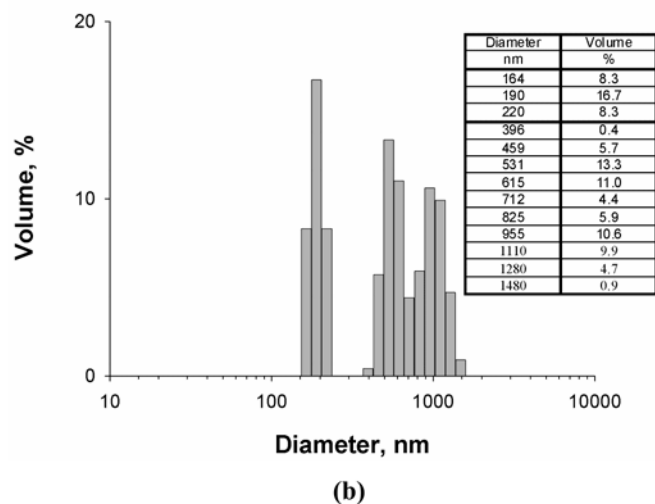
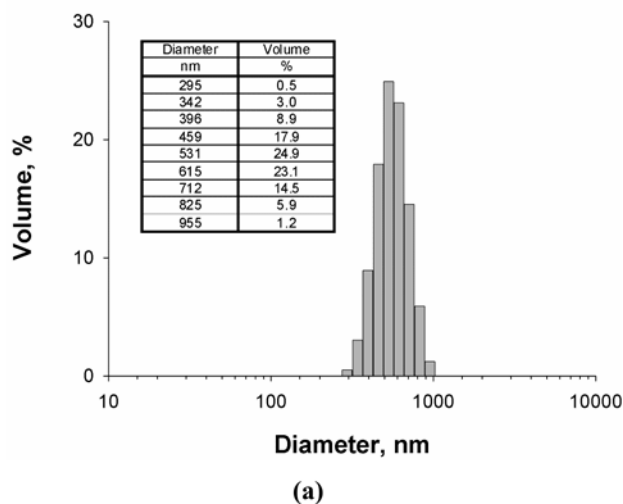


Figure 5. Particle size distributions determined by Zetasizer Nano ZS of the CuO-SiO₂ oxide composites precipitated using 5% solution of sodium silicate and 7% solution of copper(II) sulfate at (a) 40°C or (b) 60°C

reveals two bands covering the ranges 164 ÷ 220 nm and 396 ÷ 1480 nm. The greatest volume contribution of 16.7% comes from the particles of 190 nm in diameter.

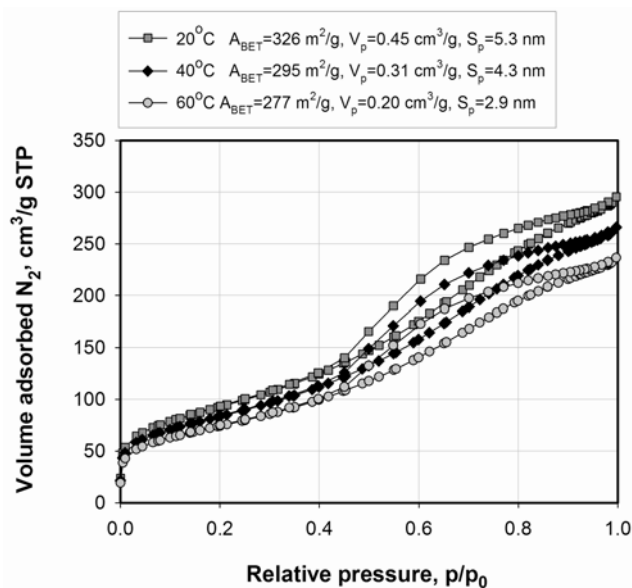


Figure 6. Nitrogen adsorption isotherms evaluated for selected CuO-SiO₂ composites

Figure 6 presents the nitrogen adsorption/desorption isotherms estimated for the composite samples obtained. The character of the isotherms indicates their mesoporous structure. With increasing the temperature the amount of nitrogen adsorbed decreases; for the samples precipitated at 20, 40 and 60°C at $p/p_0=1$ it is 295, 271 and 243 cm³/g. The surface area (BET) of the composites is relatively large and with increasing the temperature of precipitation it decreases; for the samples precipitated at 20°C and 60°C the surface area decreased from 326 m²/g to 277 m²/g. Increase in specific surface area values is correlated with decreasing of the mean size of particles.

Subsequent tests were made to check the effect of volume excess of one of the reagents on the physico-chemical properties of the oxide composites obtained with the use of 5% solution of sodium silicate and 7% solution of copper(II) sulfate at 20°C.

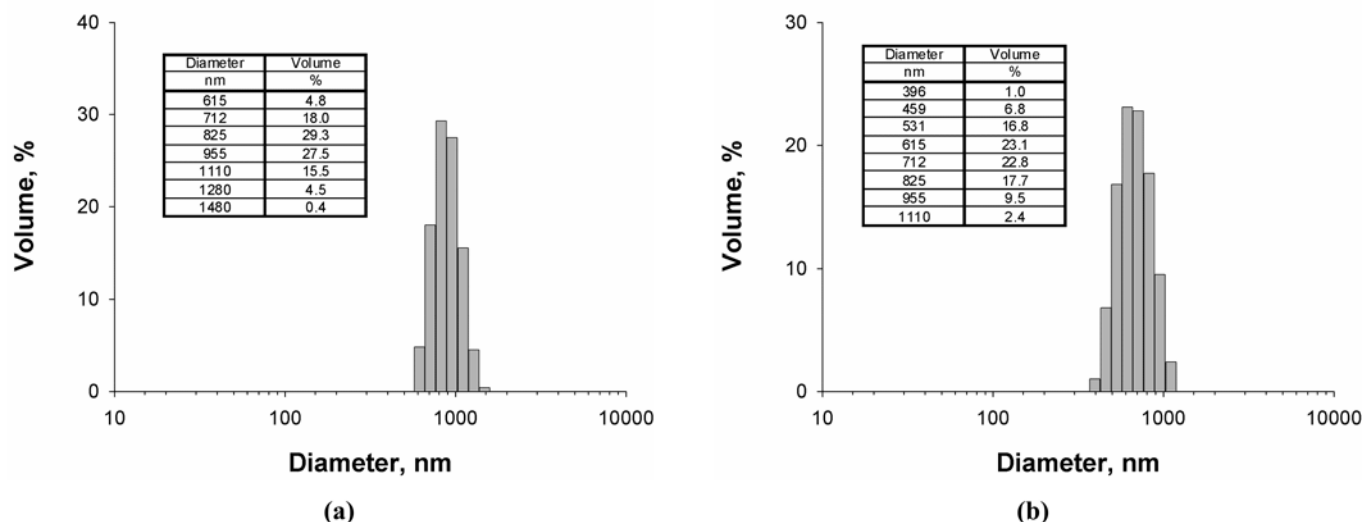


Figure 7. Particle size distributions determined by Zetasizer Nano ZS of the CuO-SiO₂ oxide composites precipitated using 5% solution of sodium silicate and 7% solution of copper(II) sulfate at the twice volume excess of (a) copper salt and (b) sodium silicate

Figure 7a presents the particle size distribution for the sample precipitated when using a twofold volume excess of CuSO₄. It shows a single band covering the diameters from the range 615 ÷ 1480 nm. The particles of 825 nm in diameter bring the greatest volume contribution of 29.3%. The particle size distribution for the sample precipitated with the twofold volume excess of sodium silicate (Fig. 7b) also shows a single band covering the range 396 ÷ 1110 nm, and the greatest volume contribution of 23.1% brought by the particles of 615 nm in diameter. The polydispersity index of the sample obtained with the twofold volume excess of CuSO₄ is 0.298, while that of the sample precipitated with the twofold volume excess of sodium silicate is much higher, of PdI=1.000.

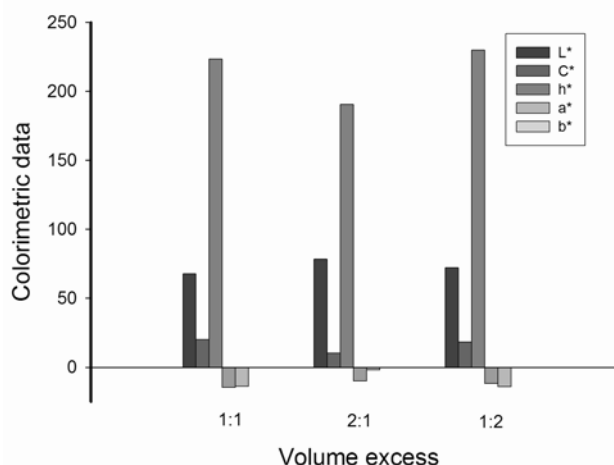


Figure 8. Colorimetric characteristics of the CuO-SiO₂ composites precipitated using 5% solution of sodium silicate and 7% solution of copper(II) sulfate at 20°C at the stoichiometric ratio and with twofold volume excess of one of the reagents

The colorimetric analyses of the composites precipitated with the use of one of the reagents in excess (Fig. 8) revealed significant differences in the colour parameters relative to those of the sample obtained for the reagents at 1:1 volume ratio. The oxide composites precipitated with the use of twofold volume excess of postgalvanic

copper(II) sulfate as well as those obtained with the use of twofold volume excess of sodium silicate are characterised by greater brightness (L^*) of 78.30 and 72.20, respectively, and lower contribution of green ($-a^*$) of (-10.01) and (-11.82), respectively. As to the contribution of blue ($-b^*$), the excess of CuSO₄ leads to its considerable decrease to (-1.86), while the excess of sodium silicate to its considerable increase to (-14.03). The corresponding values for the sample obtained with the reagents at the 1:1 volume ratio are $L^*=67.66$, $a^*=-14.63$ and $b^*=-13.82$.

CONCLUSIONS

A method allowing utilisation of the troublesome postgalvanic waste (CuSO₄ solution) for preparation of oxide composite CuO-SiO₂ of valuable properties has been proposed.

Analysis of the conditions of the process of precipitation of synthetic CuO-SiO₂ has shown that the concentration and volume ratio of the reagents have significant influence on the physico-chemical parameters of the products obtained. The most desired physico-chemical properties were obtained when the oxide composite was precipitated at 20°C with the use of 5% solution of sodium silicate and 7% solution of postgalvanic copper(II) sulfate at the 1:1 volume ratio.

Acknowledgements

This work was supported by the Ministry of Science and Higher Education research grant no. N N209 032738 (in the period 2010 – 2011).

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