Synthetic Sorbent Materials Based on Metal Sulphides and Oxides

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Chapter 1.1

Methodology of Synthesis

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Synthesis of Zinc, Copper, Cadmium, and Iron Sulfides and Their Sorption Properties

1.1 Methodology of Synthesis

One of the most important steps in the study on metal sulfides sorption properties was the analysis of their synthesis methods. Different methods provide different particle sizes and surface morphology; thus, it was crucial to choose the proper method. The analysis was performed for zinc sulfide as an example.

1.1.1 Overview and Classification of Synthesis Methods

Due to its wide applications and potential use in high technology field, ZnS was one of the most studied luminescence, photocatalyst, special morphology, and mesoporous materials in inorganic synthesis (Wang M. et al. 2011). Zinc sulfide nanoparticles can be prepared by different methods, such as colloidal aqueous and micellar solution synthesis method, using ultrasonic waves, microwaves (MWs), and gamma irradiation (Tiquia-Arashiro and Rodrigues 2016). Zinc sulfide can be synthesized in the form of various nanostructures, and Fang et al. (2011) point out three types of them:

- 0D nanostructures (nanocrystals of quantum dots type, core/shell nanocrystals, and hollow nanocrystals),
- 1D nanostructures (nanowires, nanorods, nanotubes, nanobelts, nanoribbons, and nanosheets), and
- 2D nanostructures.

Various surface morphologies of the ZnS particles may be obtained by different synthesis methods. To make the analysis more clear, we propose that those methods may be divided into two main groups:

- high-temperature methods (solid-state reaction or thermal evaporation of zinc powder and sulfur powder, thermal decomposition of precursors, etc.),

- synthesis from aqueous and nonaqueous solutions (solvothermal and hydrothermal methods, precipitation from aqueous solutions, etc.).

The reaction may be activated traditionally by high temperature only or by ultrasonic, or by MWs.

1.1.1.1 High-Temperature Methods

Zinc and sulfur react with each other violently to produce zinc sulfide. To obtain pure ZnS, the reaction should be performed in vacuum to prevent the oxidation processes. After the mixture of zinc and sulfur is heated, the elements react with each other at temperature range between 400°C and 600°C. The reaction is highly exothermic. Temperature at which reaction is initiated is dependent on the dispersity of components, i.e., if the particles are smaller, the reaction starts at lower temperature. The reaction may be also activated in the MW field. For instance, Manoharan et al. (2001) demonstrated the capability of MW-aided process to perform in the atomic-level doping of "activator" ions in the host lattice. Stoichiometric amounts of reagent grade zinc and sulfur powders were placed in a quartz tube, which was then evacuated at 10^{-3} Torr and sealed. The contents of the tube were exposed to MW irradiation in a kitchen MW oven. The exposure time for the complete reaction was 20 minutes. The average size of the obtained crystallites was 1 µm. Dhara et al. (2018) reported also successful synthesis of Mn-doped ZnS nanocrystals by mechanically alloying the stoichiometric mixture of elemental Zn, S, and Mn powders at room temperature under inert atmosphere of Ar using a high-energy planetary ball mill. Different proportions of cubic and hexagonal phases were obtained dependent on milling time varying from 2 to 6 hours, with the crystallite size of cubic phase between ~24 and ~40 nm and crystallite size of hexagonal phase from ~15 to ~30 nm. Since the interaction takes place at the temperatures above 400°C, this method is classified as a high-temperature one.

In the present research, the reaction started after 1–2 minutes of MW irradiation of the stoichiometric mixture of zinc and sulfur. Then the mixture heats up very quickly, in several seconds, to the temperature of 500°C–600°C. X-ray analysis informed that the obtained zinc sulfide crystallites had a structure of sphalerite. Both single-phase nanopowders and multiphase compositions perform high surface activity and agglomeration ability (Gevorkyan et al. 2019). Unlike interaction between zinc and selenium where the sintering of ZnSe particles takes place (Sofronov et al. 2013), no sintering was observed during MW-assisted synthesis of ZnS. As it is seen in Figure 1.1, the spherical agglomerated particles are formed, and their size appears to be from 50 up to 200 nm.

Solid-state synthesis is known as a very simple and cost-effective method that enables to obtain pure zinc sulfide nanoparticles (Jothibas et al. 2017). In our research, the infrared (IR) spectrum of the ZnS powder synthesized in the MW field out of zinc and sulfur did not show the absorption bands, as it is seen in Figure 1.2, which proved its high purity. In the IR spectrum, only
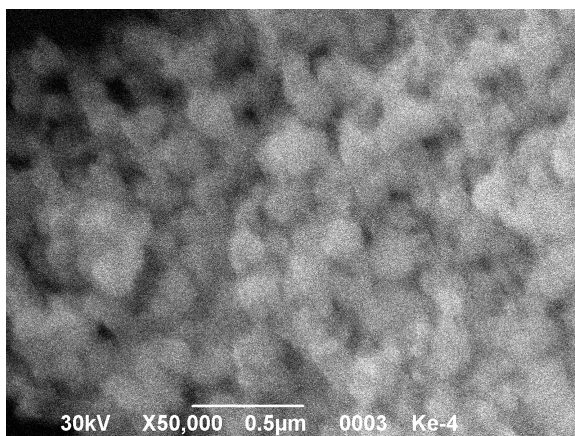
FIGURE 1.1
SEM image of the ZnS particles obtained with MW activation. MW, microwave; SEM, scanning electron microscope.
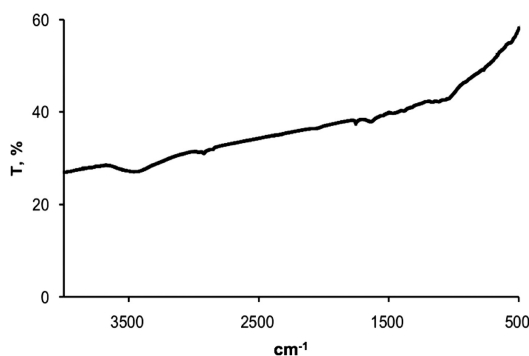
FIGURE 1.2
IR spectrum of the ZnS powder obtained in the MW field. IR, infrared; MW, microwave.

a weak absorption can be observed in the range of 3,200–3,700 cm^{-1}, which was obviously related to the stretching vibrations of water molecules. These molecules were present due to the application of potassium bromide during the IR spectrum analysis.

To reduce the exothermic effect, the well-established technique of chemical vapor deposition (CVD) is applied. CVD methods of zinc sulfide can be separated into static and dynamic methods, as well as transport methods and conventional methods. The standard dynamic ZnS CVD process as practiced today involves a liquid zinc metal that combines with hydrogen sulfide gas in a higher-temperature deposition area (McCloy and Tustison 2013, p. 34). In the CVD method with Zn and S powder as precursors, both substances are loaded into a quartz tube at some distance from one another. In a low-temperature area of the tube, also a substrate or mandrel is placed,

so the zinc sulfide can deposit on it. Then the tube is evacuated and heated up to 400°C–800°C, and the carrier gas is injected (usually nitrogen or argon).

Zhuo et al. (2008) reported that with a gas transport method at 650°C, the ZnS nanowires of 50–80 nm diameter and several dozens of microns long were obtained on the aluminum substrate. When the process temperature was increased up to 700°C, the length of nanofibers decreased down to several microns, which turned the nanofibers into a nanorods. The use of graphite substrate caused the forming of nanowires with diameter ca. 50 nm. Similarly, nanowire arrays of cubic zinc sulfide were synthesized on zinc foil by a simple thermal evaporation route at substantially lower temperature, below 500°C (Biswas et al. 2008). Interesting structures of manganese-, copper-, and cobalt-doped ZnS nanotowers are reported to be obtained on Si substrate at 750°C (Zhang et al. 2007).

Zinc sulfide may be obtained also from decomposition of some organic zinc complexes. For example, the polycrystalline ZnS nanotubes with diameters between 140 and 250 nm and the length up to tens of microns were obtained by using metal–organic chemical vapor deposition (MOCVD) template method out of the bis(diethyldithiocarbamate) $[Zn(S_2CNEt_2)_2]$ at temperature 400°C (Zhai et al. 2006).

1.1.1.2 Solvothermal Decomposition Method

The method is used in order to obtain nanosize particles from high-temperature thermal decomposition of the compounds in the environment of high boiling organic solvents. Dependent on the solvent nature and initial components, as well as on the synthesis temperature and activation method, particles of various dimensions and shape can be obtained, such as nanorods, spheres, nanowhiskers, and so on. Geng et al. (2009) reported the synthesis of Cu^{2+}-doped ZnS nanorods of 4 nm diameter and 15 nm length using a solution-phase thermal decomposition molecule precursor route at the following conditions: inert environment, oleylamine at 270°C, and reaction time 7 hours. Zhai et al. (2012) reported preparation of rod-, dot-shaped, and quasi-cubic ZnS nanocrystals using oleylamine as coordinating solvent, zinc stearate as Zn precursor and sulfur powder, and thiourea and dodecanethiol as S precursors, respectively. However, when thiourea and dodecanethiol took place of sulfur powder, no nanorods but dot-shaped and quasi-cubic ZnS nanocrystals were formed.

Pure and uniform hexagonal-phase ZnS nanorods with diameters 7–30 nm were synthesized by solvothermal decomposition of zinc diethyldithiocarbamate, $Zn-(DDTC)_2$, in hydrazine hydrate aqueous solutions at 150°C–200°C during 3–48 hours (Zhang et al. 2006). During decomposition of zinc dithiocarbamate in ethanol at 150°C–200°C, hexagonal-phase particles of spherical ZnS are formed, and their dimensions are 30–60 nm (Zhang et al. 2005). Others reported (Abdullah et al. 2016) that the precursor was decomposed to hexagonal zinc sulfide after 2–6 hours of calcination duration at 400°C, and the sizes of zinc sulfide nanoparticles were about 6–11 nm. The existence of

the hexagonal ZnS phase was not affected by the calcination duration. Sun et al. (2008) performed MW decomposition of zinc diethyldithiocarbamate at 110°C obtaining the ZnS particles size of 5 nm. ZnS particles of two shapes were reported to be obtained from thiourea solutions at a thermal heating (70°C–90°C) and MW irradiation (Sofronov, Sofronova et al., 2013). The dimensions of agglomerated particles of the spherical shape were 50–100 nm (particle size in agglomerates of 3–5 nm), whereas the length of hexagonal columns was up to 2 µm and diameter 80–100 nm.

Li Y. et al. (2008) proposed a microemulsion-assisted solvothermal process to obtain ZnS nanospheres with rough surface of cubic modification with lattice constant $a = 5.414$ Å. Zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was used as starting material, and thiourea (($NH_2)_2CS$) as the source of S, whereas cyclohexane served as the continuous oil phase, cetyltrimethylammonium bromide (CTAB) as the surfactant, 1-pentanol as the cosurfactant. The process lasted for 16 hours at temperature 120°C. Theoretically, diameter of the nanoparticles is directly proportional to the size of the microemulsion water pools, which can be expressed by the water-to-surfactant ratio ($v = [H_2O]/[\text{surfactant}]$). When the v value changed from 8, to 16, 24, and 32, the average diameter of ZnS nanosphere samples changed from 200, to 250, 350, and 1500 nm, respectively. When the temperature rose up to 180°C, the diameters of nanospheres with rough surface increased up to 1.25 and even to 3 µm.

When zinc sulfate is contracting with $Na_2S_2O_3$ in cyclohexane with CTAB at 160°C during 12 hours, nanowires of zinc sulfide were obtained of cubic crystal system. The length of the particles was several micrometers, and diameter was 30–50 nm (Dong et al. 2007). ZnS microflowers composed of numerous nanowires with a cubic structure were reported to be synthesized in water below 100°C using an inorganic capping agent $K_2S_2O_7$ (Jaffres et al. 2017). Aguilar et al. (2017) proposed a synthesis of cubic-phase ZnS using synthesized *hydrozincite* $Zn_5(CO_3)_2(OH)_6$ as a novel zinc precursor in hydro- or solvothermal method.

Wurtzite structure of ZnS nanowires was obtained when zinc nitrate contracted with thiourea within the polyethylene glycol (PEG) gel and water at 172°C during 4 days (Cheng et al. 2006). The Ag_2S-catalyzed zinc sulfide nanowires were reported to have a wurtzite structure with a width in the range of 30–80 nm and length of ca. 1 µm (Kim et al., 2018).

Unlike in the case of solvothermal synthesis, in hydrothermal method, water is applied as a solvent. The process is carried out in an autoclave and takes place at increased pressure and temperature. Wang et al. (2017) reported preparation of ZnS nanoparticles by hydrothermal method using zinc nitrate [$Zn(NO_3)_2 \cdot 6H_2O$] and thiourea [$SC(NH_2)_2$] as sources of Zn^{2+} and S^{2-} ions and CTAB [$CH_3(CH_2)_{15}N^+ (CH_3)_3 \cdot Br^-$] as a surface active agent. Hydrothermal synthesis may be initiated by MWs as well (Yan et al. 2013). Anand et al. (2009) proposed optimization of hydrothermal method for the synthesis of ZnS nanoparticles. The nanoparticles were stabilized using hexamethylenetetramine (HMTA) as a surfactant in aqueous solution, and

average grain size of the nanoparticles of the order of 2 nm was obtained. Chanu et al. (2017) reported synthesis of zinc sulfide (ZnS) nanospheres using amino acid, L-histidine as a capping agent by hydrothermal method. A particle size of 5 nm was obtained after 3 hours at the temperature 120°C. Other paper reported production of the spherical ZnS nanoparticles with diameter 100–300 nm from the reaction between zinc chloride and $Na_2S_2O_3$ at temperature 200°C during 4 hours (Jiang et al. 2007). Addition of acrylic amide C_3H_5NO caused the increase of the particle diameters up to 3 μm. When the process was performed in the conditions of MW activation, the monodisperse spherical particles of sphalerite structure ($a = 5.406$ Å) were obtained with diameter ca. 100 nm (Yao et al. 2008). It was also proposed to apply thioacetamide (Zhu et al. 2001), thiourea (Chen et al. 2003), and sodium sulfide (Li W. et al. 2008) as reagents in the hydrothermal synthesis.

Precipitation from a water solution appears to be advantageous because of the simplicity of method and its high productivity. For example, it was reported that pure and Ni (0.5%–2.0%)-doped ZnS nanoparticles were prepared by an inexpensive solid-state reaction method (Jothibas et al. 2018). A solution method for preparing oxygen-doped ZnS colloidal nanocrystals was demonstrated by Wang et al. (2018), where optimal power conversion efficiency (PCE) of the device based on ZnO/ZnS(O) reached 8.85%. The average size of the nanoparticles was ca. 8.5 nm. Song et al. (2008) reported that pure as well as Mn- and Cu-doped zinc sulfide was obtained from the reaction between zinc ethylenediaminetetraacetate and thioacetamide at 60°C–100°C. The dimensions of particles varied between 50 and 1000 nm, dependent on the synthesis temperature and thioacetamide concentration. The smallest particles were obtained at the temperature 60°C and molar ratio TAA:Zn^{2+} = 1:1.

The Mn-doped particles of ZnS (5%–20% in mass) with dimensions 2.5–4 nm were obtained by Wang et al. (2008) in the Ar atmosphere during 30 minutes. Xiao and Xiao (2008) proved that when the thioglycolic acid (TGA) is added, the particles size will be decreased down to 1.2–2.5 nm. Labiadh et al. (2017) reported that undoped and Mn-doped ZnS nanoparticles (with 5%, 10%, and 20% of Mn dopant) were synthesized at 95°C in basic aqueous solution using the nucleation doping strategy. Tripathi et al. (2007) reported synthesis of Mn-doped ZnS nanocrystals via aqueous solution precipitation method with hydrogen sulfide at room temperature in the air atmosphere during 5 hours. Obtained $Zn_{1-x}Mn_xS$ ($x = 0\%–5\%$) nanoparticles of cubic modification had sizes in the range of 4–6 nm.

Mei et al. (2017) proposed a facile MW-assisted aqueous route using sodium citrate and TGA as dual stabilizer in order to synthesize Cu–In–S/ZnS quantum dots with the size of 3.8 nm. Zinc sulfide (ZnS), various concentrations of Cu^{2+} (0.25%–1.25%)-doped ZnS, and ZnS:Cu^{2+} nanoparticles capped with various surfactants were reported to be successfully synthesized by a chemical precipitation method in ambient air at 80°C (Murugadoss 2013). The formation of a cubic phase was confirmed for all samples, and average size of the particles ranged from 3.2 to 5.3 nm.

Nanoparticles ZnS(Cu) were obtained from thiourea solution with additions of triethanolamine (TEA) and sodium polyphosphate (Kim et al. 2006; Lee et al. 2004). In other papers, precipitation of ZnS(Cu) was proposed using sodium sulfide (Corrado et al. 2009; Bol et al. 2002). Similarly, precipitation with sodium sulfide enabled to obtain nanoparticles of ZnS(1%Ag) using 3-mercaptopropionic acid (3-MPA) as a stabilizer (Jian et al. 2006).

In this chapter, the methods of metal sulfides synthesis were chosen on the basis of following requirements and assumptions:

- simple technology,
- avoidance of complicated and specific apparatus for synthesis,
- high productivity,
- potential for further increase of the process scale in order to produce larger amounts of the material.

After the thorough analysis, it was assumed that the method best meeting those requirements and providing metal sulfides for further utilization as sorbents was precipitation of them out of the aqueous solutions. As reagents, thiourea and sodium sulfide were chosen.

1.1.2 Methodology and Equipment

MW-activated synthesis was performed using an MW apparatus MARS (CEM Corporation Matthews, USA). The system uses integrated sensor technology to recognize the vessel type and the sample number in order to apply the appropriate amount of power. It has contactless in situ temperature measurement, is equipped with sensors that detect vessel type and count, and provides hundreds of preprogrammed methods.

The specific surface area (SSA) was determined with the method of thermal desorption of argon (10% argon mixture with helium) with chromatographic analysis. As a standard, the samples of aluminum oxide were used with the SSA of 4.2 and $52\,m^2/g$. The weighed sample (0.05–0.1 g) was placed in a U-tube with inner diameter 4 mm and heated during an hour in the stream of argon of flow speed of $100\,cm^3/min$ at 100°C during 1 hour. This operation served for cleaning the surface and pores from the contaminations and moisture. After that, the gas was replaced by the mixture of 10% argon in helium, and flow speed was reduced down to $50\,cm^3/min$. The gas mixture is then passed through a katharometer. The tube with the sample was placed in liquid nitrogen where it was until the end of adsorption process indicated by the return of katharometer to the initial (zero) point. It lasts ca. 2–3 minutes. Next, the tube with the sample was placed in water at room temperature where desorption of argon takes place, and the katharometer's indication went to opposite direction. The area under desorption peak is proportional to the overall amount of desorbed argon. It is assumed that the argon adsorption at 77 K has a monolayer

characteristics; thus, the area under peak is assumed to be proportional to the absolute surface of the sample. Along with each sample, the standard was measured, i.e., exact weighed sample of Al_2O_3 with known SSA. Two respective U-tubes with measured sample and the standard were connected in series.

Adsorption experiments were performed using the model solutions containing ions of investigated metals at the temperature 20°C (±1°C). Measurement of the metals concentration in the solutions before and after sorption was performed with the inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Moore 1989). The device was iCAP 6300 Duo made by Thermo Fisher Scientific.

The iCAP 6300 uses a simple pressure-controlled nebulizer gas flow or an optional factory-fitted nebulizer gas mass flow controller. Duo version of the instrument enables both radial and axial view. The device applies spectrometer of Echelle type, 52.91 grooves/mm ruled grating, 383 mm effective focal length, and 9.5° UV-fused silica cross-dispersion prism. The wavelength range is 166–847 nm, spectral bandpass is 7 pm at 200 nm, and the device uses high-performance CID86 chip detector. Plasma gas flow is fixed 12 L/min argon, and nebulizer gas is under pressure control from 0 to 0.4 MPa. Auxiliary gas has four fixed flows: 0, 0.5, 1.0, and 1.5 L/min.

The IR spectra were obtained in tablets of KBr with Spectrum One FT-IR Spectrometer (made by PerkinElmer, USA). The device employs improved Michelson interferometer, self-compensating for dynamic alignment changes due to tilt and shear, incorporating high reflectivity first-surface aluminum-coated optics. The detectors are electrically, temperature-stabilized fast recovery deuterated triglycine sulfate (FR-DTGS) or lithium tantalate (LiTaO$_3$). Wavelength range is 7,800–350 cm^{-1} with KBr beam splitter, wavelength accuracy 0.1 cm^{-1} at 1,600 cm^{-1}, and resolution is 0.5 to 64 cm^{-1}. For the FR-DTGS detector, signal-to-noise ratio for KBr optics is 30,000/1 rms, 6,000/1 p-p for a 5-second measurement and 100,000/1 rms, 20,000/1 p-p for a 1-minute measurement. For the LiTaO$_3$ detector, signal-to-noise ratio for KBr optics is 7,500/1 rms, 1,500/1 p-p for a 5-second measurement and 26,000/1 rms, 5,000/1 p-p for a 1-minute measurement.

As for nontransparent powder sample, it is difficult to obtain the absorption spectrum, the diffuse reflection spectrum was used to calculate the bandgap of materials (Kaihara and Sato 2000). It should be remembered that the diffuse reflection spectrum always contains both absorption and reflection spectral components (Nishikida et al. 1995). The relationship of the intensity of the reflected radiation to the concentration is usually presented as follows (Byrn et al. 2017):

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} = \frac{Ac}{s} \tag{1.1}$$

where R is reflectance, k is the absorption coefficient, s is the scattering coefficient, c is the concentration of the absorbing species, and A is the absorbance.

Based on the obtained spectra, the bandgap E_g for the examined material was assessed (Katrunov et al. 2010).

Structural characterization of materials was performed with X-ray powder diffraction technique using Siemens D500 X-ray Diffractometer (XRD), with Ni-filtered Cu sources and graphite-diffracted beam monochrometers. In this work, the diffraction patterns were recorded in the 2θ angle range between 10° and 110° at room temperature, with steps of 0.02° and counting time of 10 s at each point.

Particle shape and size are two concepts that are intrinsically connected (Pons and Dodds 2015). Thus, to evaluate morphology of obtained powders, scanning electron microscope (SEM) and transmission electron microscope (TEM) were applied.

The SEM was JSM-6390LV made by Jeol Ltd. (Japan) with a high resolution of 4.0 nm. The JSM-6390 specimen chamber can accommodate a specimen of up to 150 mm in diameter. Standard automated features include autofocus/autostigmator, autogun (saturation, bias, and alignment), and automatic contrast and brightness. Magnification is ×8 to ×300,000 (at 11 kV or higher) and ×5 to ×300,000 (at 10 kV or lower). The TEM was device of ПЭМ-125 type made by SELMI (Ukraine).

The results of measurement and analysis are presented and discussed in the respective chapters, for each presented method.

1.1.3 Procedures and Reactions

The solutions were prepared using the following precursors: $Cu(NO_3)_2 \cdot 3H_2O$, $CuSO_4 \cdot 5H_2O$, $CuCl_2 \cdot 3H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $CdSO_4 \cdot H_2O$, $CdCl_2 \cdot H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $ZnSO_4 \cdot 7H_2O$, $ZnCl_2$, thiourea, and aqueous solution of ammonia. All the reagents were qualified as chemically pure. All solutions were made using the distilled water.

Precipitation of the zinc, copper(II), and cadmium was performed from 0.1 and 1 M solutions of nitrate, chloride, and sulfate of the respective metal. To the volume of 1 mL of the metal salt solution, the aqueous solution of ammonia was added, or 0.1 M solution of sodium hydroxide until the require pH was reached. The value of pH was varying between 8 and 12. Next, thiourea (Th) was added in proportion of $c(\text{Th}):c(\text{Me}^{2+})$ 1:1, 2:1, or 4:1. The mixture was then heated up to boiling temperature and boiled during 1 hour. After synthesis, the obtained precipitate was filtered out, washed with distilled water, and dried at the room temperature during 24 hours.

MW-activated synthesis was performed using a MW apparatus MARS (CEM Corporation, Matthews, USA). Volume 50 mL of 0.1 M solution of zinc, cadmium, or copper(II) nitrate, chloride, or sulfate of basicity pH = 8, 10, and 12 was placed in a 250 mL glass. Then the thiourea was added in molar proportion Me^{2+}/Th 1:1, 1:2, or 1:4 with continuous stirring. Next, the mixture was placed in the viala of volume 100 mL and underwent MW activation during 30 minutes at temperature 100°C and 150°C. After the synthesis was
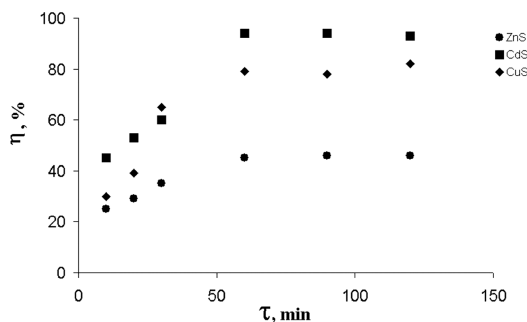
FIGURE 1.3
Percentage of the synthesized sulfides versus precipitation time from thiourea solution for the proportion $c(Me^{2+})$:$c((NH_2)_2CS)$ 1:1, pH 11.5.

finished, the obtained precipitate was filtered out, several times washed with distilled water, and dried at the room temperature during 24 hours.

The synthesis time was selected based on the assumption of maximal amount of the final product. Figure 1.3 presents the experimental graph of precipitation time for metal sulfides precipitated with thiourea in proportion $c(Me^{2+})$:$c((NH_2)_2CS)$ 1:1 and pH 11.5.

The experimental data proved that the precipitation time between 10 and 30 minutes provides small amounts of the final products. When increased up to 60 minutes, the time becomes sufficient for obtaining 45%, 79%, and 94% of zinc, cadmium, and copper(II) sulfides, respectively. Further prolongation of the synthesis time has no substantial impact on the product amount. Thus, it was assumed that the basic synthesis time using thiourea solutions was 1 hour.

Iron sulfide was obtained from the thermal reaction between sulfur and iron. Stoichiometric quantities of those substances were placed in the quartz ampule, which was then evacuated with a vacuum pump during 30–40 minutes until the pressure reached 1.3 Pa (10^{-2} mmHg). Next, the ampule was sealed and placed in the oven to be heated up to 600°C at speed of 30°C per hour. The ampule stayed in the temperature 600°C for 5 hours, and then the temperature was risen to 800°C. After 4 hours in the temperature of 800°C, the ampule was cooled down to the room temperature and opened, and the obtained substance was milled in a porcelain mortar.

Acknowledgment