

Effect of CuS, Mn₃O₄ and CeO₂ additives on Co(II) sorption by ZnS particles

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ZnS particles modified with Mn₃O₄, CeO₂ and CuS were obtained from aqueous solutions. It was shown that addition of copper and manganese ions into the reagent mixture doesn't have any influence on particle formation from thiourea solutions (the spherical particles with diameter of 0.2–0.8 μm were obtained). Introduction of CeO₂ (0.5–1 wt.%) favors particle size decrease up to 0.1–0.3 μm. Using Mn₃O₄, CeO₂ for modification proved to be ineffective in enhancing Co sorption capacity of ZnS particles. Addition of CuS (1 wt.%) into the particles leads to the increase of Co uptake from 5.0 up to 23.0 mg/g owing to formation of ZnS/CuS core-shell structures with preferential cobalt ions sorption onto CuS surface.

Keywords: zinc sulphide, metal removal, cobalt sorption, sorption capacity.

Из водных растворов получены частицы сульфида цинка с добавками Mn₃O₄, CeO₂ и CuS. Установлено, что введение ионов меди и марганца при синтезе частиц сульфида цинка не оказывает влияние на формирование частиц из тиомочевинных растворов (образуются сферические частицы с размерами 0.2–0.8 мкм). Добавление 0.5–1 мас.% CeO₂ способствует уменьшению размера сферических частиц до 0.1–0.3 мкм. Показано, что добавки Mn₃O₄, CeO₂ не позволяют увеличить сорбционную емкость частиц сульфида цинка по отношению к кобальту. Введение 1 мас. % CuS повышает сорбционную емкость частиц сульфида цинка по отношению к кобальту от 5.0 до 23.0 мг/г, что связано с образованием core-shell структур ZnS/CuS и протеканию процесса сорбции ионов кобальта на поверхности сульфида меди.

Вплив домішок CuS, Mn₃O₄ та CeO₂ на сорбційну місткість часток ZnS у відношенні до кобальту. *Д.С.Софронів, А.О.Орешина, Е.Ю.Брилева, О.М.Софронова, П.В.Матейченко, А.Н.Пузан.*

З водних розчинів отримано частки сульфиду цинку з домішками Mn₃O₄, CeO₂ та CuS. Встановлено, що додавання іонів міді або марганцю при синтезі часток сульфиду цинку не впливає на формування часток з тіосечових розчинів (утворюються сферичні частки з розмірами 0.2–0.8 мкм). Додавання 0.5–1 мас.% CeO₂ сприяє зменшенню розміру сферичних часток до 0.1–0.3 мкм. Показано, що введення домішок Mn₃O₄ та CeO₂ не дозволяє збільшити сорбційну місткість часток сульфиду цинку у відношенні до кобальту. Введення 1 мас. % CuS підвищує сорбційну місткість часток сульфиду цинку у відношенні до кобальту від 5.0 до 23.0 мг/г, що пов'язано з утворенням core-shell структур ZnS/CuS та протіканню процесу сорбції іонів кобальту на поверхні сульфиду міді.

1. Introduction

Purification of natural waters and technological liquid-waste drains of industrial activities from heavy metals is one of the main topics of sustainable development. Particular attention is paid to radionuclides removal. To solve this problem, a number of approaches have been suggested. Among them, sorption technique is commonly applied as a simple and effective method. In the view of this, development of the new sorption materials with tailored properties and improved performance is a challenging issue.

Metal sulphides were shown to be promising materials for extraction of heavy metals and radionuclides from aqueous media [1–5]. In particular, ZnS particles are characterized by the high recovery efficiency (95–97 %) towards copper, cadmium, europium and cerium ions within the pH range of 4–9. With the maximum sorption uptake achieved at pH 5, the sorption capacity for europium, strontium and cobalt is 15.5 mg/g, 8.03 mg/g and 5.56 mg/g, respectively [4].

Sorption properties of materials can be substantially increased by introducing substances that have high sorption affinity towards the target ions. Thus, copper sulphide particles were demonstrated to be highly effective material for europium and iron ions sequestration within the pH range of 5–9 [5]. The sorption capacity at pH 6 for europium, cerium and cobalt ions is 18.3 mg/g, 18.2 mg/g and 23.7 mg/g, respectively. In turn, manganese oxides [6–8] possess the super sorption characteristics which provide an excellent opportunity for the material modification. Thus, it was reported that resin-based composite extracts cadmium with 100 % efficiency within the pH range of 3–8 (sorption capacity more than 77 mg/g) [9]. In the MnO₂/CNTs system, the extraction of lead in the pH range 4–7 reaches 98 % with a sorption capacity of 78.7 mg/g at pH 5 and manganese dioxide content of 30 % [10]. When the concentration of manganese is reduced to 10 %, the sorption capacity is reduced to 57 mg/g (the sorption capacity of pure carbon nanotubes is about 30 mg/g). The introduction of manganese dioxide particles into the zeolite favors increase of the sorption capacity towards copper and lead by a factor of 2 [11]. Cerium dioxide particles are also used as an additive to increase the sorption properties. In the presence of CeO₂ cobalt sorption by clays (montmorillonite and

kaolinite) is notably increased [12]. Thus, the study of effect of additions of copper, manganese and cerium on the sorption properties of zinc sulphide particles is of a considerable interest.

The aims of the present study are to obtain particles of zinc sulphide with additions of manganese, cerium and copper, to study their chemical composition and to investigate cobalt sorption onto the synthesized particles.

2. Experimental

ZnCl₂, thiourea, aqueous ammonia, MnSO₄·5H₂O, Ce(NO₃)₃·6H₂O, CuCl₂·2H₂O, Na₂S·9H₂O were used to prepare the solutions. All chemicals were of analytical grade.

Synthesis of zinc sulphide particles was carried out by precipitation reaction using sodium sulphide and thiourea according to the procedure described earlier [4]. The content of Mn₃O₄, CuS and CeO₂ additives was established to be 1 and 10 % by weight. The resulting powders were washed several times with distilled water and dried at the room temperature for 48 h.

Sorption study was performed in a batch mode using the simulated solutions. Briefly, 0.1 g of the sorbent was put in contact with 50 mL of the feed solution with pH of 5.5. The resulting mixture was allowed to equilibrate for 40 min. The concentration of the metal in the initial solution was varied from 5 to 150 mg/dm³.

X-ray phase analysis of the powders is carried out by powder diffractometer Siemens D500 in copper radiation with a graphite monochromator on the secondary beam. Full-profile radiographs are measured in the angular interval of 10 < 2θ < 90° in steps of 0.02 and the accumulation time of 10 sec at each point. Investigation of the morphology of the surface of the resulting powders is carried out using scanning microscope (SEM) JSM-6390LV. pH is measured with pH-meter-millivoltmeter pH-150 with a glass electrode ESL-63-07 and an auxiliary chlorine silver electrode EVL1MZ. Determination of the metals concentration before and after sorption was carried out using inductively coupled plasma atomic spectrometer TRACE SCAN Advantage from Thermo Jarrell Ash (USA). IR spectra were obtained by Fourier spectrophotometer SPECTRUM ONE (PerkinElmer) in tablets of potassium bromide.

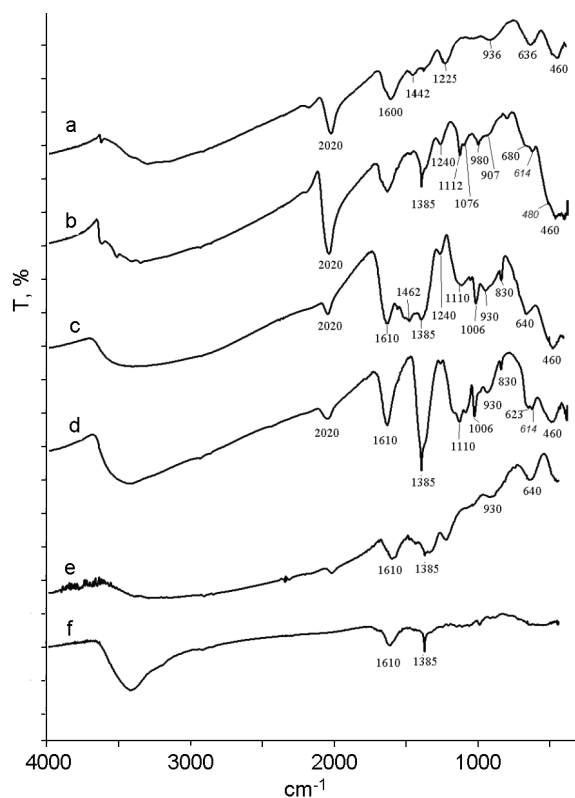


Fig. 1. IR spectra of ZnS particles obtained by precipitation with thiourea (a, b, e) and sodium sulphide (c, d, f) with 1 % (a, c), 10 % (b, d) addition of manganese and no additive (e, f).

3. Results and discussion

According to the XRD analysis, X-ray amorphous precipitates are formed after precipitation from thiourea solution with sodium sulphide.

IR spectra of the synthesized zinc sulphide powders with manganese additions are presented in Fig. 1. A broad absorption band in the region of 3000–3600 cm^{-1} and an absorption band in the range of 1600–1610 cm^{-1} , associated with valence and deformation vibrations of water molecules are observed in all the spectra. In the IR spectrum of the powder obtained without additives from the thiourea solution (Fig. 1e), absorption bands at 1385, 1240, 930 and 640 cm^{-1} are observed. In the IR spectrum of the powder obtained by precipitation with sodium sulfide (Fig. 1f), only an absorption band at 1385 cm^{-1} can be isolated. The absorption band of 1385 cm^{-1} is observed in all spectra and is associated with vibrations of NO_3^- ion adsorbed on the particle surface. In the IR spectra of the samples obtained with the addition of manga-

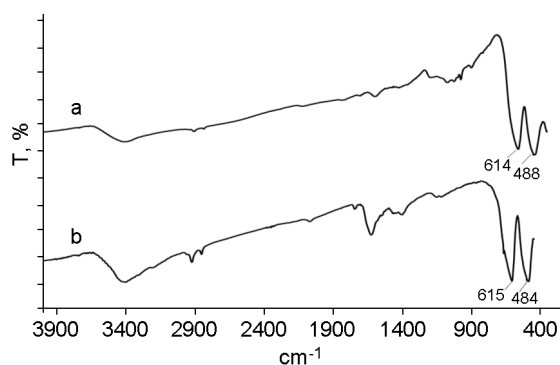


Fig. 2. IR spectra of manganese oxide particles obtained by precipitation with thiourea (a) and sodium sulphide (b).

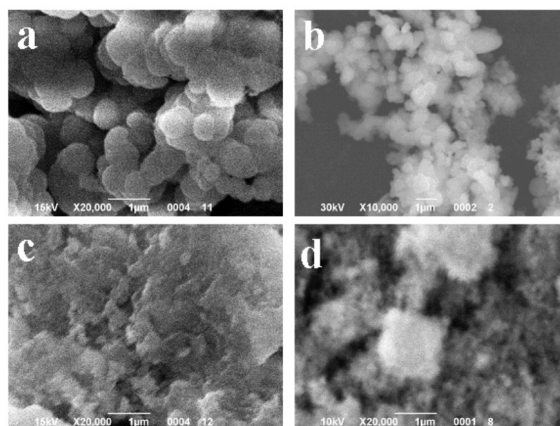


Fig. 3. Microphotographs of particles obtained by precipitation with thiourea (a, b) and sodium sulphide (c, d) with addition of 1 (a, c) and 10 % (b, d) manganese (in terms of Mn_3O_4).

nese from the thiourea solution (Fig. 1a), additional absorption bands are observed at 1442, 1225, and 460 cm^{-1} . As the concentration of manganese in the sample increases (Fig. 1b), additional absorption bands with maxima at 1112, 1076, 980, 680, 614, 480 cm^{-1} appear. In the IR spectra of the samples obtained with manganese by precipitation with sodium sulfide (Fig. 1c,d), the absorption bands with maxima at 1110, 1006, 930, 640, 623, 614, 460 cm^{-1} take place. The absorption bands at 1442, 1076 and 936 cm^{-1} apparently corresponds to the oscillation of the CO_3^{2-} anion, the formation of which is connected with the processes of carbonization of alkaline solutions. The absorption band at 640 cm^{-1} can be attributed to the vibrations of OH^- [15] groups, and the absorption band of 460 cm^{-1} is related to the vibration of Zn–O bond [5]. The absorption bands at 1112, 1006, 830, 623 cm^{-1} can be attributed to the vibrations

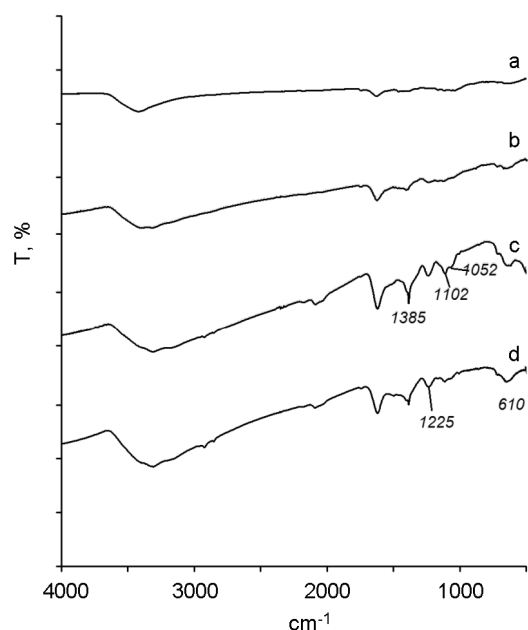


Fig. 4. IR particles of with additions of copper (a, b) and cerium (c, d) obtained from precipitation from thiourea solution with additive content of 1 (a, c) and 0.5 % (b, d) (in terms of CuS and CeO₂, respectively).

of sulfate ions [13] adsorbed on the surface of particles due to the presence of manganese sulfate residuals. The absorption bands of 680, 614 and 480 cm⁻¹ were observed for the samples with high manganese content and correspond to oscillation of Mn–O bond. The presence of absorption bands with maxima of 614 and 480 cm⁻¹ is characteristic for the oscillation of the Mn–O bond in Mn₃O₄ [14].

To confirm formation of Mn₃O₄ as a result of precipitation of the zinc sulphide particles with manganese additives, a separate reaction of manganese sulfate with thiourea and sodium sulfide was carried out. In the IR spectra of synthesized particles (Fig. 2), the intense absorption bands of 488 and 614 cm⁻¹ are observed. According to X-ray diffraction analysis, the synthesized powders contain the main phase — Mn₃O₄ resulting from the oxidation of manganese hydroxide or manganese sulfide by ambient oxygen during the drying of the powders.

The photomicrographs of the obtained particles are shown in Fig. 3. The particles of a spherical shape with diameter of 0.4–0.7 μm (average size 0.6 μm) are formed from the thiourea solution, and when depos-

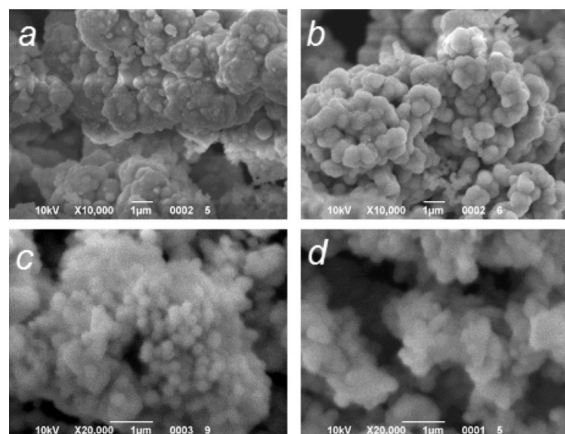


Fig. 5. Microphotographs of ZnS particles with additions of copper (a, b) and cerium (c, d) obtained from precipitation from thiourea solution with additive content of 0.5 (a, c) and 1 % (b, d) (in terms of CuS and CeO₂, respectively).

ited with sodium sulphide — with a size of less than 100 nm.

According to the X-ray diffraction analysis, the zinc sulfide particles with copper addition (1 and 10 wt.% in relation to CuS) precipitate represents a mixture of zinc sulphide with the structure of sphalerite and copper sulphide with the structure of covellite. In addition, when precipitating zinc sulphide particles with cerium (0.5–1 % by weight in relation to CeO₂), only reflections that are related to the sphalerite modification of zinc sulphide are recorded in the roentgenogram. In the IR spectrum of the ZnS particles with 1 and 10 % content (Fig. 4a,b), practically no absorption bands in the spectrum are observed. This type of IR spectrum is characteristic for pure CuS particles obtained from thiourea solutions [5]. The co-precipitation of zinc and copper sulfides apparently leads to formation of copper sulfide shell on the ZnS particles surface which prevents the formation of oxygen-containing impurities (carbonates, hydroxides, etc.). Evidently, the formation of core-shell structures of ZnS/CuS is reflected in the IR spectrum of zinc sulphide particles with addition of 0.5 % by weight of cerium (in relation to CeO₂) yielding absorption in the region of 3000–3600 cm⁻¹ and absorption band of 1620 cm⁻¹ associated with the valence and deformation vibrations of water molecules (Fig. 4d). Also, weak absorption bands with maxima of 1385, 1225, 1102 and 610 cm⁻¹ are recorded, which refer to the nitrate (1385 cm⁻¹), sulfate (1225, 1102 and

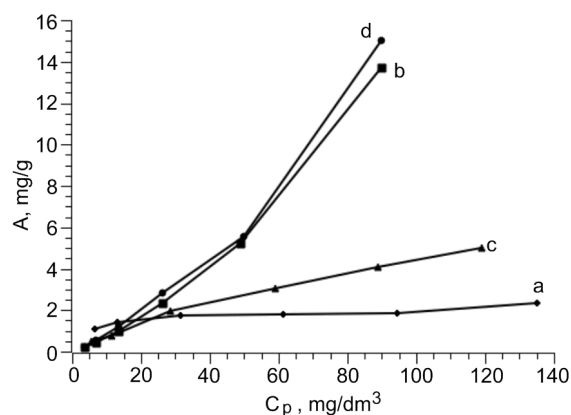


Fig. 6. Isotherms of sorption of cobalt on ZnS particles obtained by precipitation with thiourea (a, b) and sodium sulphide (c, d) with addition of 1 (a, c) and 10 % (b, d) Mn_3O_4 .

610 cm^{-1}) ions. With increase in the content of the cerium dioxide additive to 1 wt.%, increase in the absorption bands of 1385 and 1102 cm^{-1} is observed in the IR spectrum and the absorption band at 1052 cm^{-1} is recorded, which can be attributed to the carbonate ions vibrations.

Microphotographs of zinc sulphide particles with additions of cerium dioxide and copper sulphide are shown in Fig. 5. In the case of copper sulphide addition, the spherical particles with dimensions $0.2\text{--}0.8\text{ }\mu\text{m}$ (Fig. 5a,b) are formed, and when cerium dioxide is added, the particles with dimensions of $0.1\text{--}0.3\text{ }\mu\text{m}$ (Fig. 5c,d) are obtained.

The recorded sorption isotherms are presented in Fig. 6 and 7. The obtained data were treated by the Langmuir equation and the fitting results are shown in the Table. Zinc sulphide particles with additions of cerium and manganese oxides are characterized by moderate sorption capacity values for cobalt ions: for Mn_3O_4 — $2\text{--}5\text{ mg/g}$, and for CeO_2 — $6\text{--}9\text{ mg/g}$. The sorption capacity of the pristine zinc sulphide precipitated with thiourea is 5.6 mg/g (for spherical particles with size of $0.1\text{--}0.2\text{ }\mu\text{m}$) [4]. The change in the particle size (from less than 100 nm to $0.7\text{ }\mu\text{m}$) of zinc sulphide with additives Mn_3O_4 and CeO_2 also did not significantly change the sorption capacity. For particles with size of less than 100 nm (the particles with additions of Mn_3O_4 obtained by precipitation with sodium sulfide), $0.1\text{--}0.3\text{ }\mu\text{m}$ (the particles with addition of cerium dioxide) and $0.4\text{--}0.7\text{ }\mu\text{m}$ (the particles with addition of 10 % by weight Mn_3O_4 ,

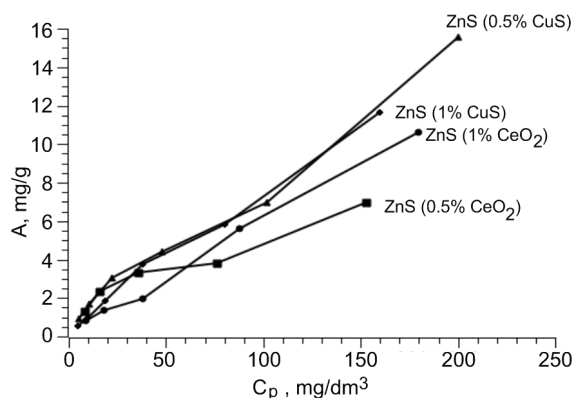


Fig. 7. Isotherms of sorption of cobalt on ZnS particles with additions of copper sulfide and CeO_2 .

obtained from the thiourea solution) A_∞ value of the order of $5\text{--}6\text{ mg/g}$ was obtained. Thus, the modification of ZnS particles with manganese and cerium oxides does not allow increasing the Co sorption efficiency.

When copper sulfide is used, a significant increase in the sorption capacity of zinc sulfide particles up to 12.5 and 23.0 mg/g is observed at CuS content of 0.5 and $1\text{ wt.}\%$ respectively. The size of these particles is larger ($0.8\text{ }\mu\text{m}$) as compared to zinc sulphide particles with Mn_3O_4 and CeO_2 additives. The crucial increase in the particles sorption performance up to 23 mg/g is associated with formation of the core-shell ZnS/CuS structures and sorption of cobalt predominantly occurs on the surface of copper sulphide (the cobalt sorption

Table. Values of the sorption capacity (A_∞) with respect to cobalt and correlation coefficient (R^2), calculated using the Langmuir model

Sample	$A_\infty, \text{mg/g}$	$R^2, \%$
ZnS(1 % Mn_3O_4)*	2.5	95.8
ZnS(10 % Mn_3O_4)*	5.0	99.9
ZnS(1 % Mn_3O_4 **)	5.1	99.6
ZnS(10 % Mn_3O_4 **)	5.2	99.7
ZnS(0.5 % CuS)*	12.5	99.5
ZnS(1 % CuS)*	23.0	99.8
ZnS(0.5 % CeO_2)*	6.6	97.8
ZnS(1 % CeO_2)*	9.0	99.6

* — the particles obtained from a thiourea solution; ** — particles obtained by precipitation with sodium sulphide.

capacity of the copper sulfide particles is 23.7 mg/g [5]).

4. Conclusions

Zinc sulphide particles with additions of Mn_3O_4 , CeO_2 and CuS were prepared by precipitation from aqueous solutions.

Formation of Mn_3O_4 as a product of precipitation from thiourea solution or under precipitation by sodium sulfide occurs due to oxidation of manganese hydroxide or manganese sulfide by ambient oxygen during the drying of the powders.

Introduction of copper and manganese into the reaction mixture does not affect the size of the spherical ZnS particles derived from thiourea solutions. With cerium used as an additive, the size of the spherical particles is reduced to 0.1–0.3 μm .

The addition of manganese and cerium does not significantly affect cobalt sorption capacity of the particles, and the change in the sorption capacity of the doped particles can probably be due to change in their specific surface area.

The addition of 1 % by weight of copper sulphide provides notable increase of the sorption capacity of the zinc sulphide particles for cobalt, which is attributed to for-

mation of core-shell ZnS/CuS structures and predominant cobalt uptake by copper sulphide.

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