

## THE SYNTHESIS OF CRYSTALLINE, MONO-PHASE COPPER AND ZINC ARSENATES (III)

This research is part of a continuing effort to synthesize copper and zinc arsenates(III) to use as a zinc dust activator in zinc sulphate solution purification. In this paper, the feasibility of synthesizing crystalline, mono-phase zinc and copper arsenates(III) were investigated. Copper and zinc arsenates(III) were prepared by adding their sulphate solutions into arsenious solution obtained by dissolving  $As_2O_3$  in NaOH aqueous solution. The structure and crystal lattice of the products and amount of the elements in precipitations were characterized by X-ray diffraction(XRD) and Atomic Absorption Spectrometry(AAS), respectively. Based on the results of XRD in the conditions of NaOH concentration = 1 mol/L,  $n(OH^-)/n(As) = 1:1$ ,  $n(Cu)/n(As) = 1:2$ , reaction temperature 90°C and reaction time 8h, a mono-phase crystalline copper arsenate(III) with the chemical composition of  $Cu(AsO_2)_2$  and tetragonal crystal lattice was synthesized. In these conditions, the yields of arsenic and copper precipitation from the solution were 93.81% and 97.68%, respectively. Based on the XRD results in the conditions of NaOH concentration = 1 L,  $n(OH^-)/n(As) = 1:1$ ,  $n(Zn)/n(As) = 1:2$ , reaction temperature 80°C, reaction time 2h and washing pH = 6, a mono-phase crystalline zinc arsenate (III) with the chemical composition of  $Zn(AsO_2)_2$  and monoclinic crystal lattice was synthesized. In these conditions, the yields of arsenic and zinc extraction from the solution were 77.70% and 46.37%, respectively.

*Keywords:* Synthesis; Copper Arsenate (III); Zinc Arsenate (III); Crystalline; zinc dust activator

## 1. Introduction

Arsenic is widespread in nature and can be detected in traces everywhere. On the one hand, there is about several hundred thousand tons of arsenic cycling in the steps of mining, beneficiation and smelting each year during the production process of nonferrous metals; on the other hand, arsenic and its compounds are toxic, its disposal technique is complicated and demand for it is limited. Therefore, how to effectively use and dispose of arsenic compounds is an awkward situation for many plants [1,2].

Many complex metal arsenates (III) have been identified [1]. In 18th century, the Sweden chemist Scheele firstly found copper arsenate (III) and it was used as an artist's color [1,2]. It is a mixture of copper arsenates (III) to which formulas such as  $Cu_3(AsO_3)_2$ ,  $CuHASO_3$ , and  $Cu(AsO_2)_2$  have been assigned [1]. The double salt of copper arsenate (III) and copper acetate,  $Cu(CH_3COO)_2 \cdot 3Cu(AsO_2)_2$ , is Schweinfurth green, another artist's color. Calcium and copper arsenates (III) were formerly used as "copper-arsenic liquor" to control pests in viniculture [1]. Also, in mid-19th century, a kind of pesticide mainly composed of copper arsenates (III) was firstly registered

in America [2]. At the end of 20th century, it was found out that zinc or copper arsenates (III) could be used as zinc dust activator to remove cobalt from zinc sulphate electrolyte [3-5]. Freeman et al. [3] proposed a hydrometallurgical process for the recovery of copper arsenate (III) from zinc plant cement copper residues and the use thereof in the purification of zinc electrolyte with the attendant upgrading of the copper value in the treated cement copper residue. Following them, Kangas et al. [4] described a metallurgical process for the recovery of zinc arsenate (III) from cement copper cake residues using zinc containing spent electrolyte or zinc neutral, and the use thereof in the purification of impure zinc electrolyte. Recently, it was discovered that copper arsenate (III) could be used to purify copper electrolyte [2,6-10]. The results of laboratorial experiments showed that the concentrations of antimony and bismuth in copper electrolyte decreased greatly after copper arsenate (III) was added. However, there were insufficient reports about the preparation technique of zinc and copper arsenates (III) in the world. Only Xiao et al. [2] investigate preparation of copper arsenate (III) with arsenic trioxide. The effect of variables such as  $n(OH^-)/n(As)$ ,  $n(Cu)/n(As)$ , NaOH concentration, reaction temperature and pH

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value had been examined on the yield of copper arsenate (III). The optimum conditions for preparing copper arsenate (III) were: molar ratio of alkali to arsenic 2:1, NaOH concentration 1 mol/L, molar ratio of copper to arsenic 2:1, pH value 6.0 and reaction temperature 20°C. The yield of copper arsenate was as high as 98.65% under optimum conditions, and the molar ratio of Cu to As in the product was about 5:4. Higher yield of copper arsenate (III) extraction from a solution was the main goal of Xiao et al [2] in their study. Reactants were used more than stoichiometry ratios to achieve this purpose. There was no study on whether the precipitations were amorphous or crystalline. Actually, synthesized precipitations and formed phases were not characterized in that study. Also, in their study, the effect of time, which is a very important variable, was not considered.

This study was designed to investigate the feasibility of synthesizing crystalline and mono-phase zinc and copper arsenates (III) to use as zinc dust activator in zinc sulphate solution purification [11-15]. Copper and zinc arsenates (III) were precipitated by adding their sulphate solutions into arsenious solution that was obtained by dissolving  $As_2O_3$  in NaOH aqueous solution. Also, in this study, the structure and crystal lattice of the products were identified and the amounts of the elements in precipitations were analyzed.

## 2. Experimental procedure

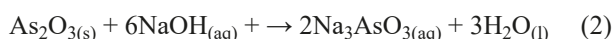
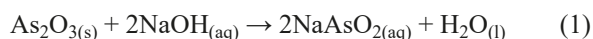
### 2.1. Materials

All the chemical reagents used in present study such as arsenic trioxide, copper sulphate, zinc sulphate, sulphuric acid (98%) and sodium hydroxide (NaOH) purchased from Merck Co., (Germany) and were of analytical grade and used as received without further purification. Deionized water was used in all experiments.

### 2.2. Synthesis and characterization

The Synthesis experiments were conducted at the desired temperature using a hot plate with magnetic stirrer and a 250 ml balloon with three necks. The solution conditions (pH and temperature) were controlled using a pH controller and thermometer (Metrohm-827 pH lab). In the experiments, the stirring speed was kept constant by setting the stirrer speed at a certain setting in order to obtain sufficient mixing of solids with the liquid phase. A water-cooled condenser was attached to the central opening of the balloon in order to prevent solution loss by evaporation.

Copper and zinc arsenates (III) were synthesized by adding their sulphate solutions into arsenious solution. As shown in Eq. (1) and Eq. (2), the arsenious solution was made by dissolving  $As_2O_3$  in NaOH solution under magnetic stirring.



After magnetic stirring at the determined temperature for a specific duration, the precipitate was separated from the solution by filtration followed by washing with hot deionized water. The precipitate was then dried in an oven at 105°C overnight. A flowchart of the procedure is illustrated in Fig. 1.

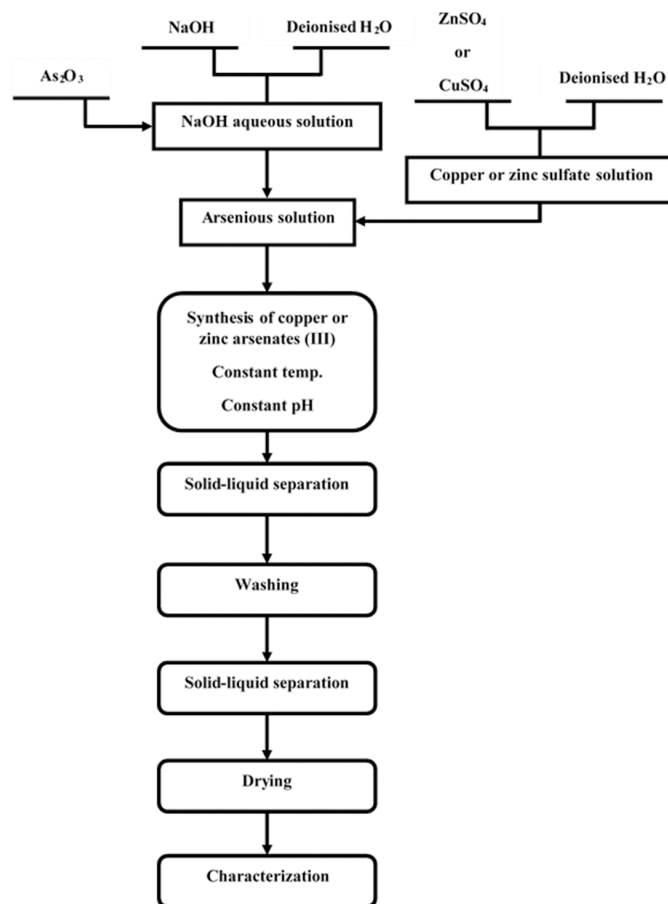


Fig. 1. Flowchart of experimental procedure

Water-washed and dried products were stocked for the XRD and AAS examinations using Philips X'Pert Pro diffractometer (XRD- D8 ADVANCED-BRUCHERS AXS model, Germany) with Cu  $K_{\alpha}$  radiation ( $\lambda = 1.54060\text{\AA}$ ) and Varian model 240AA type Atomic Absorption Spectrometry, respectively. Also, the filtrates were analysed by AAS for copper or zinc as well as arsenic.

## 3. Results and Discussion

### 3.1. Synthesize of copper arsenate (III)

The experimental conditions and results of synthesized copper arsenates (III) are given in TABLE 1. As mentioned above, Xiao et al. [2] investigated the impacts of various parameters only on the yield of copper arsenate (III) precipitate. In fact, they did not characterize precipitates and formed phases. Also, in their study, the effect of time was not addressed. The initial experiment of this study (TABLE 1 experiment No. C1) was done on the optimum conditions of Xiao et al.'s [2] examina-

Experimental conditions and results of synthesized copper arsenates (III)

No.	Experimental conditions					Results					Predicted phases	XRD analysed phases
	NaOH conc. (mol/L)	n(OH <sup>-</sup> ) to n(As)	n(Cu) to n(As)	Temp. (°C)	Time (h)	Yield of extraction %		Content of precipitation wt. %		n(Cu) to n(As) in product		
						As	Cu	As	Cu			
C1	1	2:1	2:1	20	3	79.00	62.21	25.96	33.05	3:2	Cu <sub>3</sub> (AsO <sub>3</sub> ) <sub>2</sub>	—
C2	1	1:1	1:2	80	1	75.43	99.30	40.08	23.25	2:3	CuHAsO <sub>3</sub> + Cu(AsO <sub>2</sub> ) <sub>2</sub>	—
C3	1	3:1	3:2	80	1	94.11	100	27.00	38.05	5:3	—	—
C4	1	1:1	1:2	80	4	49.61	99.95	36.07	30.80	1:1	CuHAsO <sub>3</sub>	—
C5	1	1:1	1:2	90	8	93.81	97.68	48.76	22.93	1:2	Cu(AsO <sub>2</sub> ) <sub>2</sub>	Cu(AsO <sub>2</sub> ) <sub>2</sub>

tion. Fig. 2A shows XRD pattern of the obtained precipitate under these conditions of the experiment No. C1. As shown in TABLE 1 (experiment No. C1), the molar ratio of copper to arsenic in precipitate in these conditions was about 3:2. By assuming that the precipitated compounds were only copper arsenate (III), it can be claimed that this precipitate phase was Cu<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub>. The Analysis of XRD pattern was done by X'pert HighScore software. Since this precipitate was not completely crystalline, any phases could not be attributed to this precipitate. Moreover, a similar XRD pattern was reported in Xiao et al. [2]. That XRD pattern was attributed to copper arsenate (III), but the

corresponding JCPDS was not found. Actually, the structure of copper arsenate (III) remained to be studied further. Thus, the following experiments were done to investigate copper arsenate (III) synthesis condition, trying to produce crystalline and mono-phase copper arsenate (III).

The reaction of copper arsenate (III) precipitation can occur on the basis of reactant stoichiometry ratios according to Eq. (3) to Eq. (5) as follows:

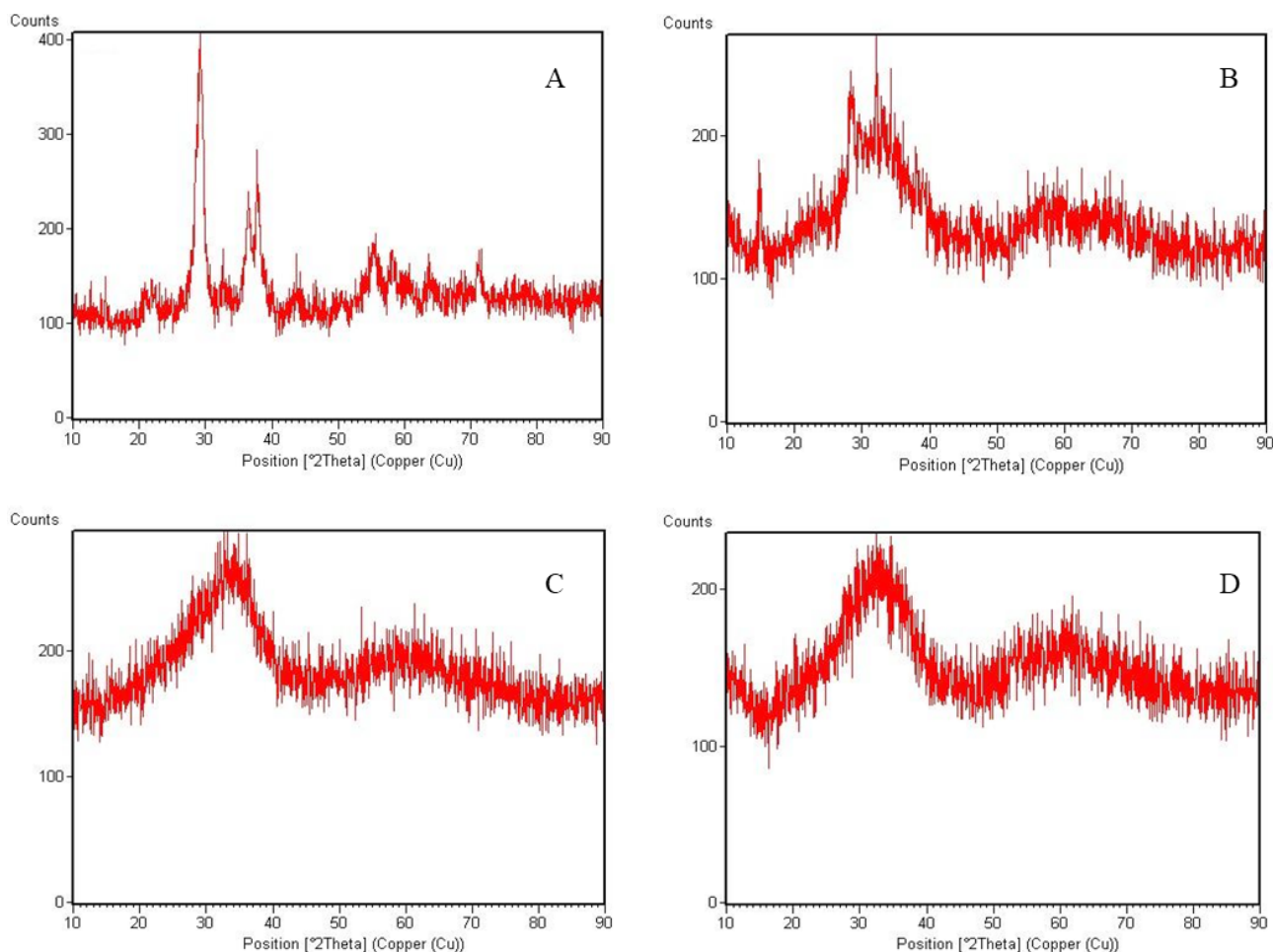
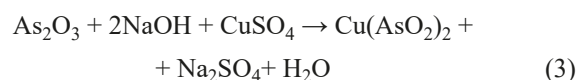
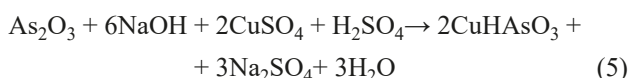
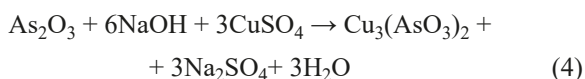


Fig. 2. XRD pattern of synthesized copper arsenates (III). A: under conditions: NaOH conc. 1 mol/L, n(OH<sup>-</sup>)/n(As) = 2:1, n(Cu)/n(As) = 2:1, pH = 6, T = 20°C and t = 3 h. B: According to Eq. (3) for 1 h. C: According to Eq. (4) for 1 h. D: According to Eq. (3) for 4 h



Reactant stoichiometry ratios of Eq. (3) and Eq. (4) were used in the experiments No. C2 and No. C3 with the reaction temperature of 80°C and reaction duration of 1h. As shown in TABLE 1, in the experiment No. C2, arsenic and copper contents in the product were 40.08% and 23.25%, respectively. Since the molar ratio of copper to arsenic in the product was about 2:3, the precipitate compound might have combined phases of  $\text{CuHAsO}_3 + \text{Cu}(\text{AsO}_2)_2$ . But in experiment No. C3, the molar ratio of copper to arsenic in the product was about 5:3, which could not be attributed to any copper arsenate (III) phase or compound of them. Since there was a high amount of sodium hydroxide in Eq. (4), some of the copper precipitated probably in the form of other phases such as copper sulphate. Also, the copper extraction from the solution was 100%, which confirm this statement. Fig. 2B and Fig. 2C show XRD patterns of the synthesized precipitations in experiments No. C2 and No. C3, respectively. There are some peaks in Fig. 2B, but it is not completely crystalline. This figure cannot be analyzed, no phase could be attributed to this pattern. Since there is not any peak in Fig. 2C, precipitation synthesized according to Eq. (4) in experiment No. C3 is completely amorphous.

In experiment No. C4, based on the reactant stoichiometry ratios of Eq. (3) and reaction temperature of 80°C, reaction time was extended to 4h. Since the molar ratio of copper to arsenic in precipitation was about 1:1, its copper arsenate (III) phase probably was  $\text{CuHAsO}_3$ . Fig. 2D shows XRD patterns of synthesized precipitation in experiment No. C4. A comparison of the Fig. 2B and Fig. 2D reveals that they look much alike, but Fig. 2B's peaks are missing in Fig. 2D. In fact, the obtained precipitation in experiment No. C4 was completely amorphous and its XRD pattern was not analyzable.

The reaction temperature and time of experiment No. C5, based on the reactant stoichiometry ratios of Eq. (3), were ex-

tended to 90°C and 8 h, respectively. The color of synthesized precipitation changed from dark green to light bluish green when reaction time elapsed more than 5 h. the yields of arsenic and copper precipitation from solution were 93.81% and 97.68%, respectively. It should be mentioned that arsenic extraction from the solution increased significantly and reached as high as 90% of extraction from a stoichiometric solution. Also, arsenic and copper contents in the synthesized precipitation reached 48.76% and 22.93%, respectively. This precipitation had the highest amount of arsenic and the molar ratio of copper to arsenic was about 1:2, so its copper arsenate (III) phase was probably  $\text{Cu}(\text{AsO}_2)_2$ . Fig. 3 shows XRD patterns of synthesized precipitation in experiment No. C5. Since this pattern's peaks were sharp, the synthesized copper arsenate (III) was completely crystalline. Also, the pattern's peaks were exactly coincident with JCPDS card of  $\text{Cu}(\text{AsO}_2)_2$ . Since there were not any extra pattern peaks, the synthesized precipitation was a mono-phase copper arsenate (III). The crystal lattice of the synthesized copper arsenate (III) was tetragonal (the related crystallographic planes are given on the pattern's peaks of Fig. 3). In the conditions of the experiment No. C5, a copper arsenate (III) was synthesized more than crystalline and mono-phase copper arsenate (III), with the lowest molar ratio of copper to arsenic. It was suitable for using in electrolyte purification not only in hydrometallurgical production of zinc but also in copper industry.

### 3.2. Synthesize of zinc arsenate (III)

The reaction of zinc arsenate (III) precipitation can occur on the basis of reactant stoichiometry ratios according to Eq. (6) to Eq. (8) as follows:

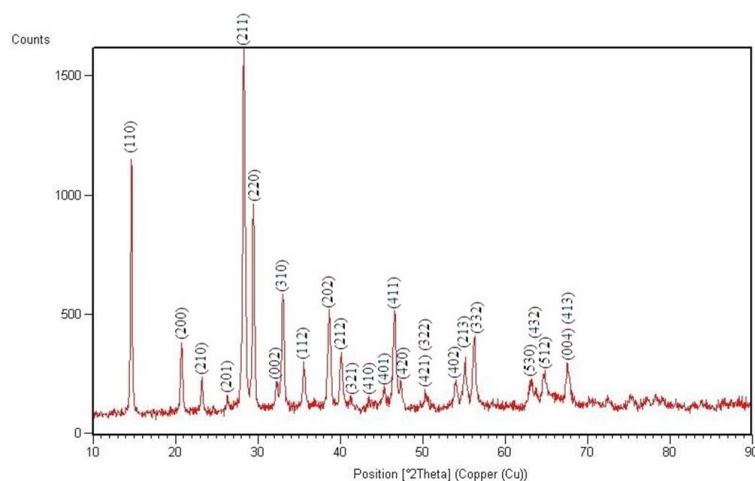
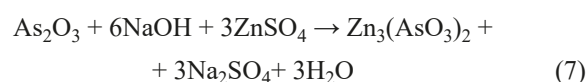
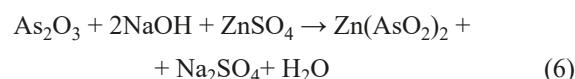
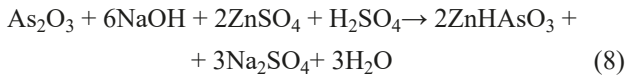


Fig. 3. XRD pattern of synthesized precipitation ( $\text{Cu}(\text{AsO}_2)_2$ ) according to Eq. (3) for 8 h



In Eq. (7) and Eq. (8), the solution contained 6 mol. of sodium hydroxide, that cause a high pH. Zinc can precipitate as basic sulphate or hydrate in high pH. In order to prevent this problem, only stoichiometry ratios of Eq. (6) was used in experiments. Experimental conditions and results of synthesized zinc arsenates (III) were given in TABLE 2.

Experiment No. Z1 of TABLE 2 was done in reaction temperature of 80°C for 4h and solution pH self-adjusted on 5.5. Content of arsenic and zinc in the synthesized precipitates were 43.84% and 29.66%, respectively. Since the molar ratio of zinc to arsenic in product was about 7:9, precipitate compound maybe were combined phases of  $\text{ZnHAsO}_3 + 3\text{Zn}(\text{AsO}_2)_2 + \text{Zn}_3(\text{AsO}_3)_2$  or  $5\text{ZnHAsO}_3 + 2\text{Zn}(\text{AsO}_2)_2$ . Fig. 4 shows XRD patterns of synthesized precipitation in experiment No. Z1. Since this pattern's peaks were sharp, synthesized zinc arsenates (III) were completely crystalline. Pattern's peaks were exactly coincident on JCPDS cards of  $\text{Zn}(\text{AsO}_2)_2$  and  $\text{Zn}_3(\text{AsO}_3)_2$ . Crystal lattice of synthesized  $\text{Zn}(\text{AsO}_2)_2$  and  $\text{Zn}_3(\text{AsO}_3)_2$  were monoclinic and orthorhombic and related main peaks were distinguished on the pattern's peaks of Fig. 4. As above discussed this precipitation was two phase, so in next experiments it will be tried to synthesize a mono-phase zinc arsenate (III). For this purpose synthesize of zinc arsenate (III) according to Eq. (6) were examined

in reaction time of 2 and 8 hour in experiments No. Z2 and No. Z3, respectively. When reaction time was 2 h, molar ratio of zinc to arsenic in product was obtained about 2:5. This ratio could not be attributed to any zinc arsenate (III) phase or compound of them. When reaction time was extended to 8h, molar ratio of zinc to arsenic in product was about 1:2. So, synthesized zinc arsenate (III) phase probably was  $\text{Zn}(\text{AsO}_2)_2$ . Fig. 5A and Fig. 5B shows XRD patterns of synthesized precipitations in experiments No. Z2 and No. Z3, respectively. Fig. 5A and Fig. 5B same as Fig. 4 were compound of two phase  $\text{Zn}(\text{AsO}_2)_2$  and  $\text{Zn}_3(\text{AsO}_3)_2$ . But by comparing intensity of phases's main peaks, it can be mentioned that intensity of peaks related to  $\text{Zn}_3(\text{AsO}_3)_2$  were decreased in Fig. 5A and Fig. 5B than Fig. 4. In fact molar ratio of  $\text{Zn}_3(\text{AsO}_3)_2$  to  $\text{Zn}(\text{AsO}_2)_2$  was decreased in precipitate. This result is in good agreement with obtained results from molar ratio of zinc to arsenic.

As above mentioned zinc can precipitate as basic sulphate or hydrate. Since the arsenic precipitated more than stoichiometry ratio of Eq. (6), it seemed probable that arsenic trioxide had formed in the product. So the pH of the washing solution effect was examined on formed phases in next experiments. Experiments were done according stoichiometry ratios of Eq. (6) in reaction temperature of 80°C for 2 h and synthesized precipitates were washed in pHs 7, 6, 5 and 4, respectively. Without using any additive washing solution pH self-adjusted on 7 that related results were given above in experiments No. Z2. But in

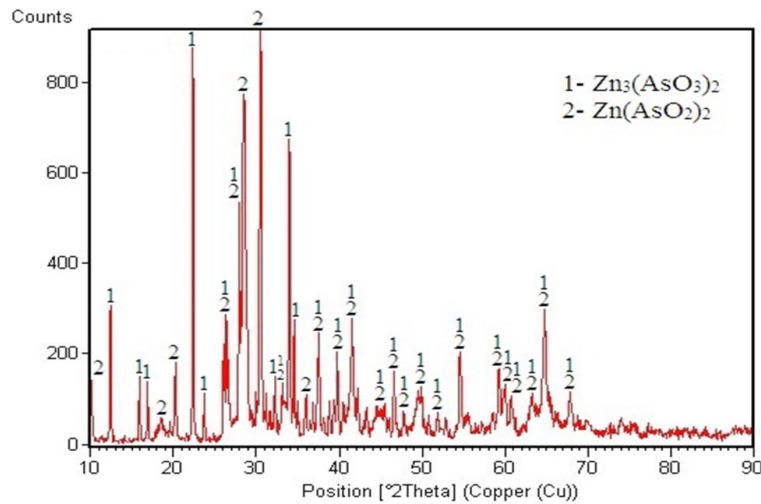


Fig. 4. XRD pattern of synthesized precipitation according to Eq. (6) for 4 h

TABLE 2

Experimental conditions and results of synthesized zinc arsenates (III)

No.	Experimental conditions						Results				
	NaOH conc. (mol/L)	n(OH <sup>-</sup> ) to n(As)	n(Zn) to n(As)	Temp. (°C)	Time (h)	Washing pH	Yield of extraction %		Content of precipitation wt. %		n(Zn) to n(As) in product
							As	Zn	As	Zn	
Z1	1	1:1	1:2	80	4	7	—	—	43.84	29.66	7:9
Z2	1	1:1	1:2	80	2	7	82.90	63.37	44.80	14.95	2:5
Z3	1	1:1	1:2	80	8	7	89.39	87.49	46.76	19.98	1:2
Z4	1	1:1	1:2	80	2	6	77.70	46.49	49.29	12.84	3:10
Z5	1	1:1	1:2	80	2	5	62.16	51.63	50.41	18.28	3:7

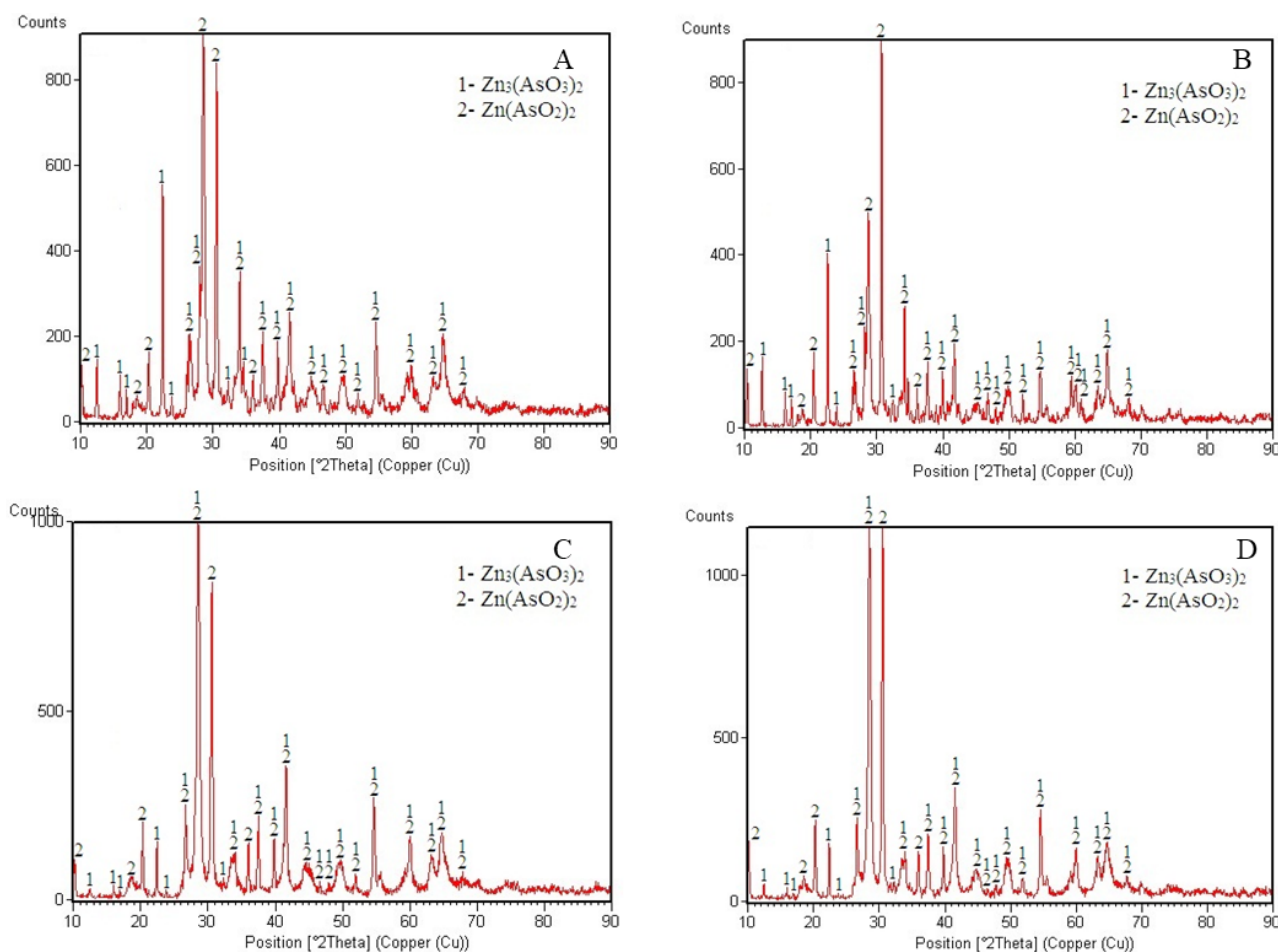


Fig. 5. XRD pattern of synthesized zinc arsenates (III) according to Eq. (6) A: For 2 h and washing pH = 7. B: For 8 h and washing pH = 7. C: For 2 h and washing pH = 6. D: For 2 h and washing pH = 5

next experiments sulfuric acid were used to decrease washing solutions pH.

By decreasing washing solution pH to 6 in experiment No. Z4, yields of arsenic and zinc extraction from solution were decreased by declining washing solution pH from 7 to 6. The molar ratio of zinc to arsenic in product was about 3:10. This ratio could not be attributed to any zinc arsenate (III) phase or compound of them. When washing solution pH was declined to 5 in experiments No. Z5, yields of arsenic and zinc extraction from solution were decreased to 62.16% and 51.63%, respectively. Also, molar ratio of zinc to arsenic in product was about 3:7. In final experiment washing solution pH was declined to 4, but in this pH all of synthesized precipitates were dissolved in solution and nothing remained as solid. Fig. 5C and Fig. 5D shows XRD patterns of synthesized precipitates in experiments No. Z4 and No. Z5, respectively. Fig. 5C and Fig. 5D same as Fig. 5A were compound of two phase  $Zn(AsO_2)_2$  and  $Zn_3(AsO_3)_2$ . But by comparing intensity of phases's main peaks, it can be mentioned that intensity of peaks related to  $Zn_3(AsO_3)_2$  were decreased significantly in Fig. 5C and Fig. 5D. In fact molar ratio of  $Zn_3(AsO_3)_2$  to  $Zn(AsO_2)_2$  was declined notably in precipitate. Since amount of formed  $Zn_3(AsO_3)_2$  was very lower than  $Zn(AsO_2)_2$ , it can be ignored. Thus, it can be said that the mono-phase zinc arsenate (III) with the chemical

composition of  $Zn(AsO_2)_2$  and monoclinic crystal lattice has been synthesized.

#### 4. Conclusions

In this study, copper and zinc arsenates (III) successfully have been synthesized by adding their sulphate solutions into arsenious solution that was obtained by dissolving  $As_2O_3$  in NaOH aqueous solution. Based on the XRD and AAS results the following conclusions may be highlighted:

- (1) In the conditions of NaOH concentration 1 mol/L,  $n(OH^-)/n(As) = 1:1$ ,  $n(Cu)/n(As) = 1:2$ , reaction temperature  $90^\circ C$  and reaction time 8 h, the mono-phase crystalline copper arsenate (III) with the chemical composition of  $Cu(AsO_2)_2$  and tetragonal crystal lattice was synthesized. Yields of arsenic and copper precipitation from solution were obtained 93.81% and 97.68%, respectively. Percentage of arsenic and copper in precipitate were 48.76 and 22.93, respectively.
- (2) In conditions NaOH concentration 1 mol/L,  $n(OH^-)/n(As) = 1:1$ ,  $n(Zn)/n(As) = 1:2$ , reaction temperature  $80^\circ C$ , reaction time 2h and washing pH = 6, the mono-phase crystalline zinc arsenate (III) with the chemical composition of

Zn(AsO<sub>2</sub>)<sub>2</sub> and monoclinic crystal lattice was synthesized. Yields of arsenic and zinc extraction from solution were obtained 77.70% and 46.37%, respectively. Content of arsenic and zinc in the synthesized precipitation were 49.29% and 12.84%, respectively.

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