JOURNAL of THE TURKISH CHEMICAL SOCIETY SECTION: A CHEMISTRY

TURKISH CHEMICAL SOCIETY

Preparation of the Nano-Sulfur from the Wastes (Foam) in the Al-Mishraq Sulfur Mine (Mosul/Iraq)

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Abstract: The research included estimating the elemental sulfur percentage in sulfuric foam waste, which was found to be 88.15%. Potassium polysulfide was prepared from this waste and used to prepare nano-sized sulfur particles through reduction processes. Stable suspensions were obtained for more than 30 days. The crystalline structure of the prepared samples was studied using X-ray diffraction (XRD). It showed a crystalline growth of nano-sized sulfur particles from the non-crystalline structure at a concentration of 0.5 mL. The crystalline bundles began to appear at a concentration of 1 mL, and their intensity increased, and good bundles appeared at a concentration of 1.5 mL. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were used to study the same prepared samples, and the particle size range was (19.59-43.47 nm), (31.33-44.23 nm), and (31.52-62.64 nm). The method was characterized by its ease, low cost, and absence of harmful environmental gas emissions.

Keywords: Foam, nano-sized sulfur, potassium polysulfide.

Submitted: September 18, 2023. **Accepted:** October 15, 2023.

Cite this: Ahmed SS, Abdulla MO, Hamdoon AA. Preparation of the Nano-Sulfur from the Wastes (Foam) in the Al-Mishraq Sulfur Mine (Mosul/Iraq). JOTCSA. 2024; 11(1): 31-8.

DOI: https://doi.org/10.18596/jotcsa.1362128.

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1. INTRODUCTION

Nanotechnology is considered one of the most important modern sciences due to its many contributions to various fields of knowledge. Nanomaterials, including sulfur, are important in fighting cancerous diseases and agricultural pests and using nano-sulfur in lithium batteries (1). In literature, many studies have focused on preparing and using nano-sulfur in several areas. For example, Guo and his colleagues successfully used ultra-small monodisperse sulfur molecules through a chemical reaction between sodium polysulfide and hydrochloric acid in a fine emulsion system (2). Deshpande and his colleagues prepared nano-sulfur from hydrogen sulfide gas (3). Xie X.Y and his colleagues added cysteine to the sulfur solution and studied the results using ultrasound waves to obtain nano-sulfur particles with different shapes and sizes (4). Chaudhuri, R. G., and Paria were able to prepare nano-sulfur using decomposition in an acidic medium of a sodium thiosulfate solution and using surface tension reducers to obtain nano-sulfur with a size of 30 nm (5) IA, M and his team studied the antifungal activity using nano-sulfur deposited from a solution of sodium sulfide The study revealed that the average particle size of the nano-sulfur used in the antifungal activity was 25 nanometers (6). Teng and his team also studied the possibility of using nano-sulfur in various fields, including environmental treatments, water and soil purification, and the manufacturing of nanodevices through nanotechnology. The study concluded that nano-sulfur's unique properties and functions could lead to many applications (7). Shevchenko and his team used a new method to prepare biocompatible and biodegradable nano-sulfur particles, which were non-toxic and had a size of 10-20 nanometers. The results showed that nano-sulfur could be used as a promising anti-cancer agent by isolating copper (8). Xu, P.F. and his team prepared nano-sulfur as a disinfectant, antifungal, and antibacterial agent (9). Meselhy and his team studied the effect of nano-sulfur on rice plants and found that it improved their growth and reduced the toxicity and accumulation of arsenic in rice (10).

2. EXPERIMENTAL SECTION

2.1. Obtaining the raw material (foam)

The raw material used in the study (foam) was obtained from the General Company for Sulphur Al-Mashraq, which is in the form of ground gray granules.

2.2. Chemical Analysis

Many chemical analyses were carried out to identify the components of sulfur foam, as well as to estimate the elemental sulfur content in sulfur residues. The percentage of sulfide ions in a solution of potassium polysulfide was also evaluated. Additionally, the free sulfur percentage in the suspended solution of nano-sulfur was calculated according to standard methods (11,12).

2.3. Preparation of Potassium Polysulfide

Due to the high sulfur content in sulfur waste (Foam), according to the analyses conducted, it is possible to prepare multiple potassium sulfides from it per standard methods (13).

2.4. Preparation of Nanoscale Sulfur from Potassium Polysulfide

0.1, 0.2, 0.3, 0.4, 0.5, 1, 1.25, 1.5, 1.75, and 2.0 mL samples of potassium polysulfide solutions were added to a liter of distilled water. After several minutes, nanoscale sulfur was observed as suspended in the solution. The solution was studied using scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy-dispersive X-ray spectroscopy (EDX).

3. RESULTS AND DISCUSSION

Nanotechnology is one of the most important fields of scientific research due to its wide range of applications and the unique properties of nanomaterials that differ from larger particles. Therefore, the study and application of nanomaterials have attracted the attention of many researchers. Based on this, we prepared nano-sulfur from the waste of sulfur foam, which is a byproduct of the chemical oxidation process used to purify in Mishraq sulfur.

3.1 The Chemical Analysis of Foam

The chemical oxidation is one of the methods used to purify sulfur in the Mishraq field, which results in sulfuric residues known as foam (14). Table 1 shows the components of these residues according to the analyses conducted.

Table 1: Components of the foam.

Parameters	wt(%)
Free Sulfur	88.15
Carbon	1.86
Ash	2.23
Acidity	1.53
Moisture	3.65
Bonded sul-fur	2.58

The elemental sulfur content in the known sulfur wastes, called "foam", reached 88.15%, which is a good percentage that can be used to introduce elemental sulfur into similar reactions to those found in pure sulfur, especially since the other materials found in the foam are inert under normal conditions.

The Energy Dispersive X-ray Spectroscopy (EDX) of sulfur wastes (foam) can be used to obtain the composition or chemical analysis of the material, as the (EDX) technique provides the nature of the elements contained in the material as well as their percentage (15). In our study, we used the EDX spectral analysis to identify the basic elements that make up the foam material, as shown in Figure 1 and Table 2.

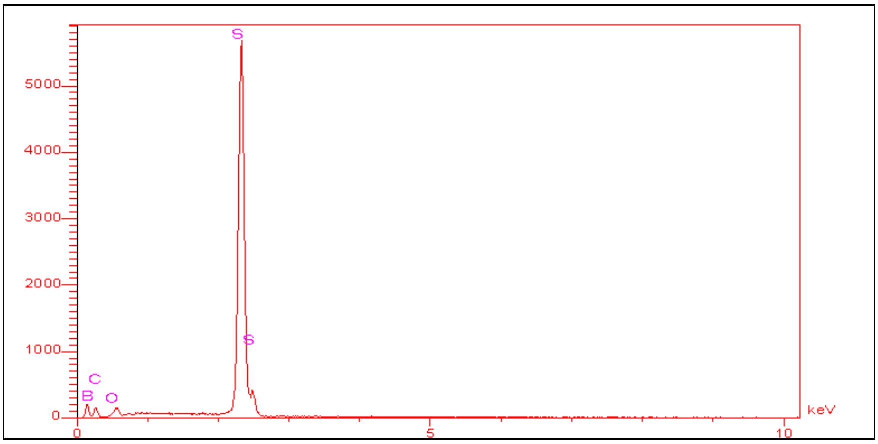

Figure 1: X-ray scattering energy spectrum of sulfur waste (foam).

Table 2: Percentages of basic elements of foam.

Element	wt (%)
S	80.90
C	16.30
O	2.80

It is clear from the table that the basic composition of foam material is sulfur, carbon, and oxygen.

3.2. X-ray Diffraction Measurements (XRD) for Foam

X-ray diffraction (XRD) technique was used to study the crystal structure of different materials (16). Table 3 and Figure 2 illustrate the results of these measurements.

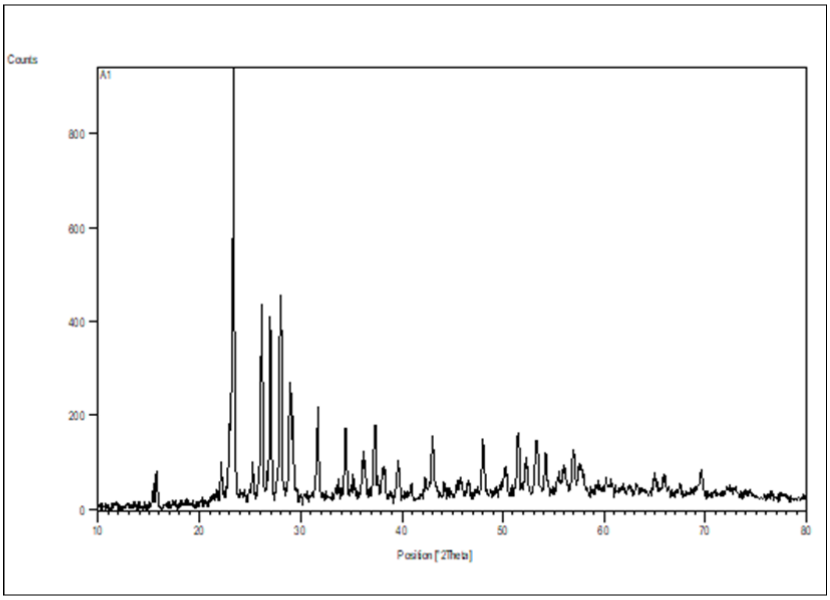

Figure 2: X-ray diffraction of foam.

Table 3: Values of diffraction angles 2θ, atomic distance d, and intensity I for foam sulfur residues.

Peak number	2θ	d-spacing	I%
1-	11.6782	7.57785	0.83
2-	15.7284	5.63446	7.59
3-	22.2128	4.00213	6.49
4-	23.3760	3.80556	100.00
5-	26.1610	3.40640	44.59
6-	28.9413	3.08518	28.06
7-	36.1583	2.48424	11.29
8-	43.0481	2.10127	13.46
9-	46.5667	1.95036	2.59
10-	48.0697	1.89283	10.67

It is evident from Figure 2 that there are 30 peaks, the most important of which are mentioned in the above table. It was also observed that there are major bundles belonging to assigned sulfur through the values of diffraction angles 2θ and atomic distance d, most notably the bundle that appeared at 2θ = 23.3760, which matches the X-ray diffraction pattern of orthorhombic sulfur. These results were compared using the X-pert High Score Plus program linked to the X-ray diffractometer.

3.3. Thermogravimetric Analysis (TGA)

TGA is a method of thermal analysis that involves monitoring changes in chemical and physical properties that occur during an increase in temperature, thereby determining the nature of the material being analyzed. This is done by assessing the stability of the materials, identifying the absorbed moisture level, and determining the amount of non-organic components that usually remain until the end of the measurement due to their high resistance to temperature. In our study, TGA measurement was used to analyze the foam material, and Figure 3 shows the results of this analysis.

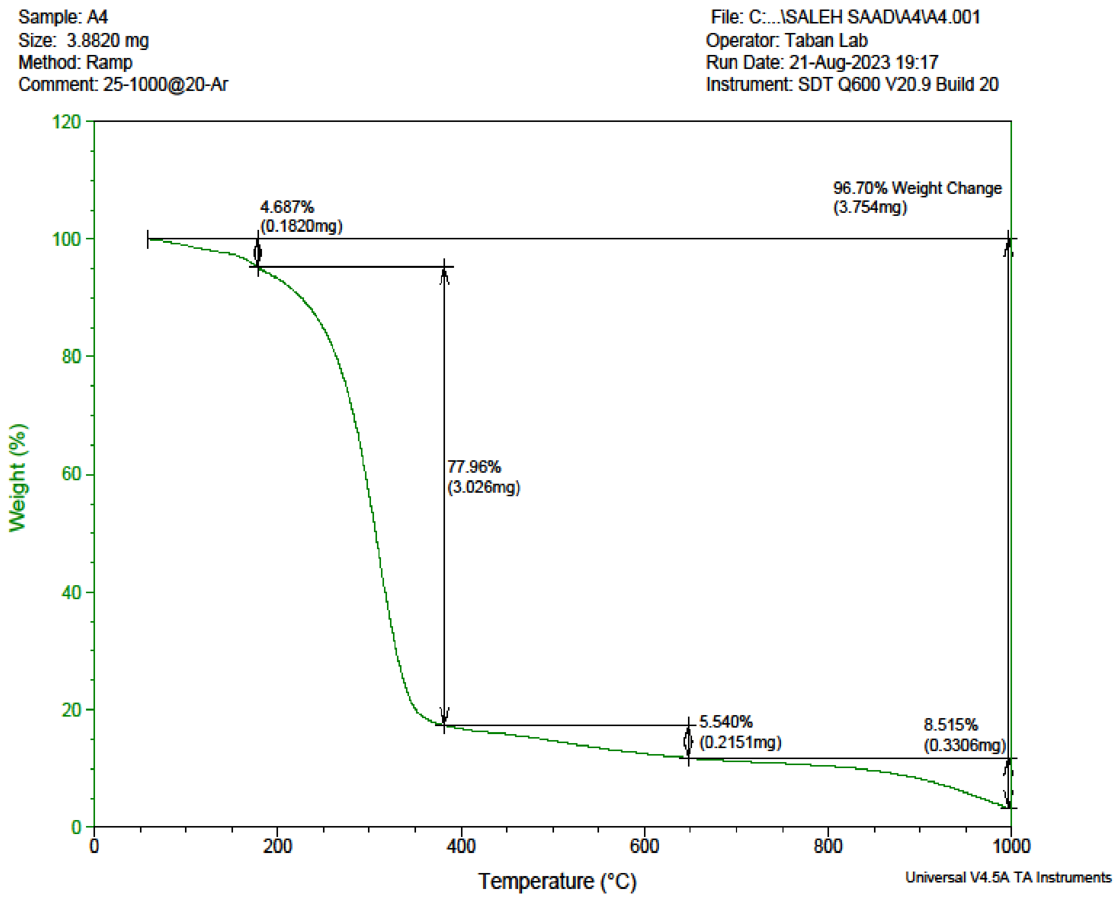

Figure 3: Thermogravimetric analysis of foam.

The measurement of the thermogravimetric analysis and through the figure showed changes in weight in four areas; at a temperature of 180 °C, the loss of moisture occurred completely, as the moisture water is immersed inside the sulfur smelter and needs more energy for getting rid of it, as the percentage of change in weight reached 4.687%. At a temperature of 375 °C, the loss of elemental sulfur occurs, as we note that the percentage of change in weight reached 77.86% at 650 °C, as there is a loss of sulfur consonant with carbon; in other words, the disintegration of carbo-sulfur compounds occurs, but at a temperature of 1000 °C, there is a loss of carbon and sulfur residues adsorbed within the fine pores, as the percentage of total weight loss reached 96.7%, while the remaining percentage, which is 3.3, represents metal oxides such as silica SiO_2, resulting from the use of slite clays in one of the stages of sulfur purification.

3.4. Preparation of Polysulfide Potassium

Since the sulfur residues foam contains a high percentage of elemental sulfur, which can react without intrinsic effects from the carbo-sulfur substances known as (carsul), which are separated by filtration, it was used in a polysulfide potassium preparation according to the following equation:

$$2KOH + carsul - xS \longrightarrow K_2S_x + carsul$$

Carsul is separated from the solution by filtration, and then the percentage of sulfide in a polysulfide solution of potassium was estimated according to approved weighing methods (11), as the percentage of sulfide in the solution was 21.1 %.

3.5. Preparation of Sulfur Nanoparticles

Very few volumes of potassium polysulfide solution were used and diluted at a certain volume of water, as after a short period (less than two minutes), turbidity of the solution (i.e., a suspended solution is formed), the solution becomes more turbid over time.

It was found through the measurements that were made that the cause of turbidity is obtaining sulfur nanoparticles by diluting potassium polysulfide using different sizes of 0.1-2 mL/L. The cessation of hydrolysis has been noted to occur when the concentration of potassium polysulfide reaches 2%. After adding this ratio to the water, the solution is vigorously agitated to achieve a uniform mixture. Subsequently, potassium polysulfide material is introduced, resulting in the formation of a suspended solution. The sulfur nano concentration was found by iodometric analysis (14), and Table 4 shows the concentration of nano sulfur.

Table 4: Sulfur Nanoconcentrations in Dilute Solutions of K_2S_x.

Sample Number	Volume (mL) K_2S_x	NPs(ppm)
1	0.1	1120
2	0.2	2094
3	0.3	2969
4	0.4	3787
5	0.5	4580
6	0.75	6150
7	1	7145
8	1.25	6430
9	1.5	3125
10	1.75	1437
11	2	0

From the table, we can see a decrease in elemental sulfur concentration, which is due to a decrease in the percentage of polysodium sulfide degradation, which stops at a 2% volume of potassium polysulfide.

All models prepared by XRD X-ray diffractometer, SEM scanning electron microscope, and EDS scattering spectrometer were studied as follows:

3.6. Scanning Electron Microscope and Dispersed Energy Spectrum of Sulfur Nanoscales

The samples prepared from sulfur nanometers were studied by SEM. The magnified images show that it has a spherical shape and that the granular size range of the sulfur nanoparticles prepared for volumes 0.5, 1.0, and 1.5 mL was, respectively: 19.59-43.47 nm and 31.33-44.23 nm and 31.52-62.64 nm as shown in Figure 4.

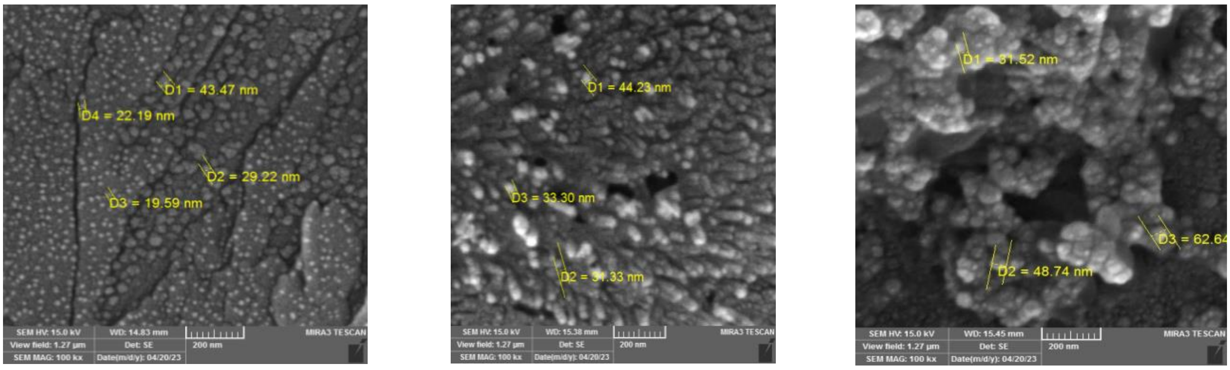

Figure 4: Scanning electron microscopy (SEM) images of diluted K_2S_x models (0.5, 1, and 1.5 mL).

The measurement of the sparse energy spectrometry of X-rays (EDX) also showed the presence of sulfur clearly in the dilute solutions, and Figure (5) and Table (5) illustrate this:

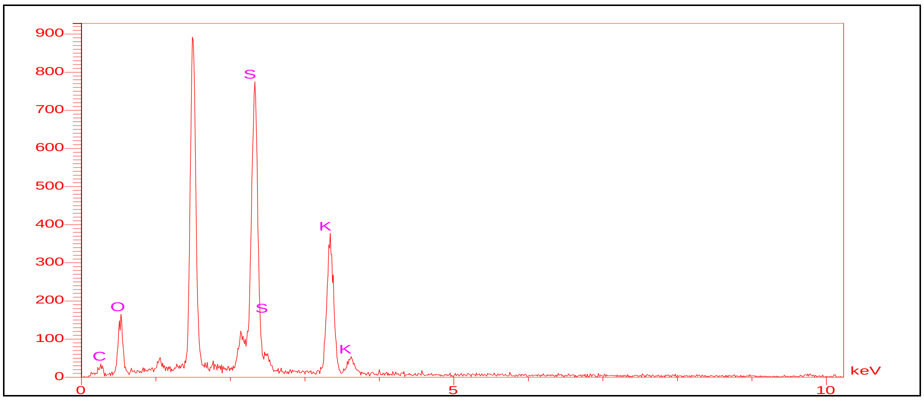

Figure 5: X-ray energy spectrum of the prepared nanoporous sulfur solution.

Table 5: The proportions of the basic elements of the prepared nano-sulfur solution.

Element	Wt(%)
S	30.56
C	13.63
O	32.31
K	23.50

We notice from the figure the presence of sulfur clearly in the suspended solution, as well as the presence of potassium and oxygen, as the preparation of nano-sulfur was through the addition of potassium polysulfide as described in the experimental section, as well as the presence of carbon mainly in sulfur residues, and this indicates that the shape accurately matches the preparation process.

3.7. X-ray Diffraction Measurement of Prepared Nano-Sulfur

The X-ray diffraction pattern of the prepared models was measured using dilution at 0.5-1-1.5 mL (6-8). The measurement result shows the following:

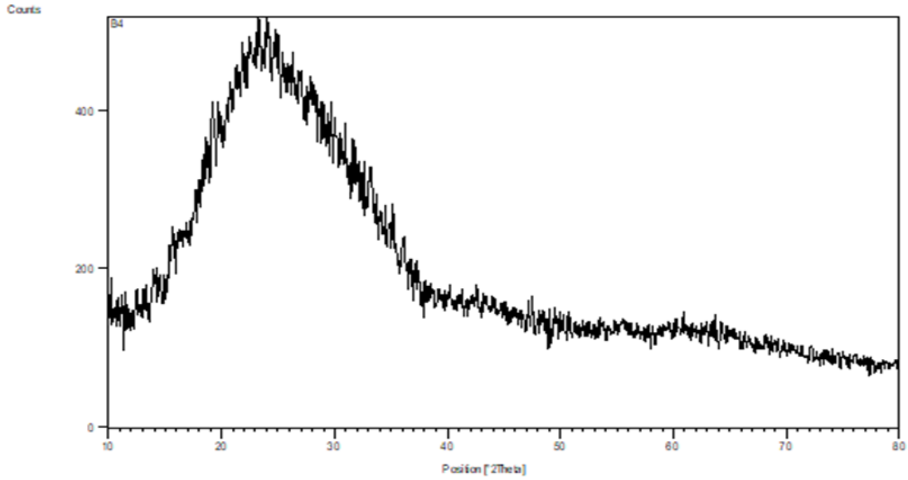

Figure 6: X-ray diffraction of nano-sulfur prepared from dilution 0.5 ml of K_2Sx solution.

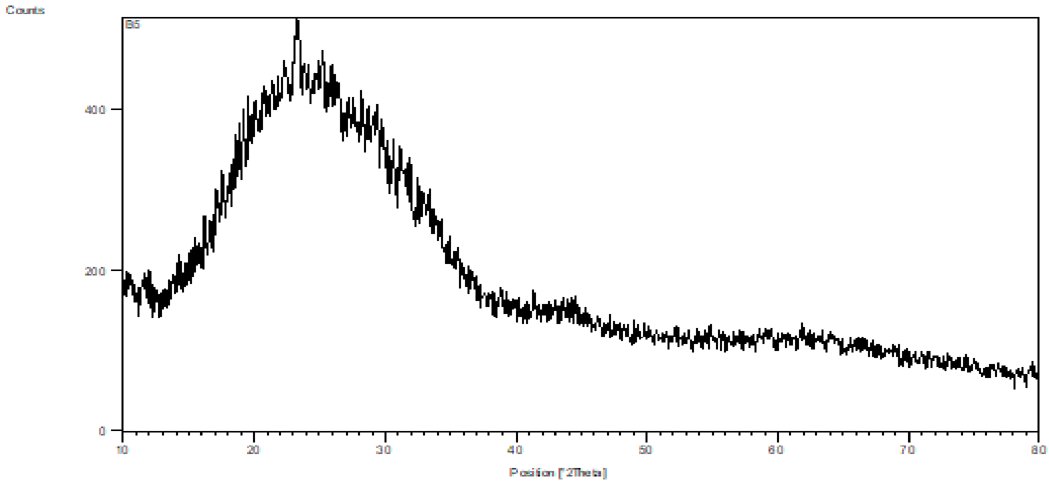

Figure 7: X-ray diffraction of sulfur nanoscale prepared from dilution of 1mL of K_2S_x solution.

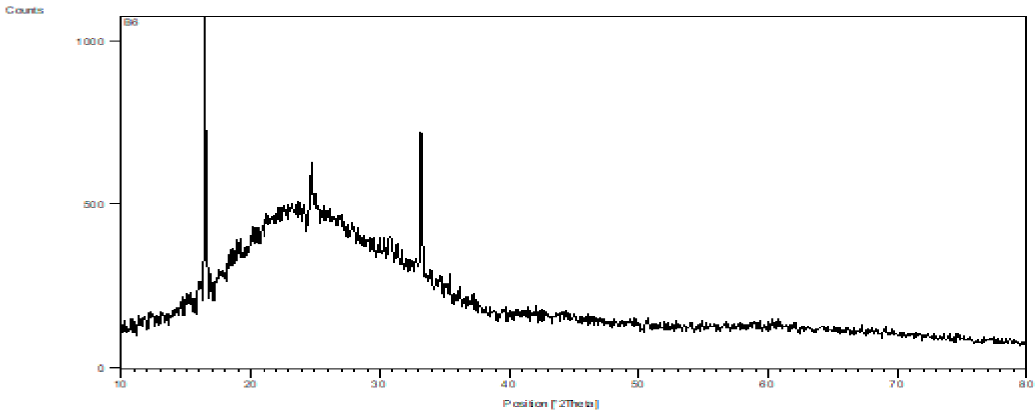

Figure 8: X-ray diffraction of nano-sulfur prepared from dilution of 1.5 mL of K2Sx solution.

We note from the three figures that by increasing the concentration from 0.5 mL / L to 1.5 mL / L there is a development in the crystal structure of the nano-sulfur resulting from dilution by moving from the amorphous structure to the crystal structure by increasing the concentration, in the concentration of 0.5 mL/L it is noted that the composition of the nano-sulfur is amorphous through the broadband 2ϴ = 20-30 as in Figure 6. At a concentration of 1 mL/L, despite the predominance of the amorphous phase, a crystal beam began to appear at ϴ = 24.73(2) as in Figure 7. While the concentration of 1.5 mL/L through Figure (8) showed that nano-sulfur is a mixture of crystalline sulfur through the three beams indicated in Table (6) and amorphous sulfur.

Table 6: Values of diffraction angles 2ϴ, atomic distance d, and intensity I For nanosulfur prepared from dilution 1.5 mL of K_2S_x solution.

Peak number	2ϴ	d-spacing	(%) I
1-	16.4514	5.38842	100.00
2-	24.7394	3.59884	17.75
3-	33.1973	2.69873	55.95

4. CONCLUSIONS

1. Solid sulfur residues resulting from the chemical method of purification of mining sulfur in Al-Mishraq contain a high percentage of elemental sulfur, which is suitable as a source of elemental sulfur instead of pure sulfur.
2. The possibility of preparing a potassium polysulfide solution from sulfur residues as a raw material.
3. Preparation of nano-sulfur without the use of contaminated chemicals.
4. Obtaining non-crystalline sulfur as one of the forms of elemental sulfur.
5. The possibility of immediate preparation of nano-sulfur in situ when used to combat agricultural pests.

5. CONFLICT OF INTEREST

There are no conflicts of interest.

6. ACKNOWLEDGMENTS

At the end of this work, we thank the University of Mosul, the College of Education for Pure Sciences, the Department of Chemistry, and the General Company for Sulfur Al-Mishraq for the facilities they provided to complete the research.

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