

## THE EFFECTS OF COPPER NANOPARTICLES ON THE PROPERTIES OF NAFTALAN OIL

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**Abstract.** Have been synthesized and stabilized of copper nanoparticles by the chemical reduction method in the presence of sodium oleate as a surfactant. XRD, SEM, and EDS analysis showed that the surface of the nanoparticles is covered with a thin layer of the copper oxide film. The size of the synthesized and stabilized nanoparticles is 14-25 nm. After the introduction of copper nanoparticles, the photoluminescent properties of various oil fractions have been studied. The photoluminescence intensity of the oil increased with the addition of small amounts of copper nanoparticles into the naftalan oil. The paper also revealed that the introduction of nanoparticles into oil leads to a decrease in the kinematic viscosity, density, and refractive index of oil.

**Keywords:** Naftalan, oil, copper, nanoparticles, luminescence, viscosity.

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### 1. Introduction

Naftalan oil is one of the crude oil types of the Azerbaijan Republic, with unique healing properties. Naftalan oil has been part of folk medicine in many countries of the East since ancient times. Due to its exceptional healing properties, it is widely included in the daily routine of practical medicine and veterinary medicine (Guliev *et al.*, 2017). The study of the physical properties of the organic materials is an important task, since their chemical properties are well studied as compare with the physical ones (Mamedaliyeva, 2022; Shevchenko *et al.*, 2022). One of the organic materials the physical properties of which are intensively studied is Naftalan oil. The properties of the healing Naftalan oil differ from that of any oil in the world, which is usually produced for industrial purposes (Adigezalova *et al.*, 2017; Babaev *et al.*, 2015; 2017). Naftalan oil can use for the treatment of many diseases of humans and farm animals. Naftalan oil also can be used in the form of baths during spa treatment and lubrication - in non-resort conditions, in the form of applications and procedures. In addition to native Naftalan oil, for different applications are quite widely used for drugs from Naftalan oil.

This paper is devoted to studying the effect of copper nanoparticles, synthesized and stabilized by the chemical reduction method, on the properties of naftalan oil. It is supposed that the introduction of nanoparticles into Naftalan oil can increase the physical and chemical properties of the oil as well as provide additional properties (Ramazanov *et al.*, 2020; Hajiyeva *et al.*, 2021).

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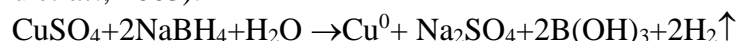
## 2. Experimental part

### 2.1. Materials

Copper sulphate ( $\text{CuSO}_4 \times 7\text{H}_2\text{O}$ , 98% chemically pure, Merck CAS № 7758-99-8); sodium tetrahydroborate ( $\text{NaBH}_4$ , 632287 Aldrich); sodium oleate (PLC Pcode  $\text{C}_{18}\text{H}_{33}\text{NaO}_2$  PLC 113655, 98% chemically pure); Naftalan oil; deionized water.

### 2.2. Synthesis copper nanoparticles

Copper nanoparticles were synthesized by chemical reduction process using copper (II) sulfate ( $\text{CuSO}_4 \times 7\text{H}_2\text{O}$ ) and sodium tetrahydroborate ( $\text{NaBH}_4$ ) as precursor substances and sodium oleate as surface-active substance according to the scheme: (Cha *et al.*, 2006; Kim *et al.*, 2006; Liu *et al.*, 2003).



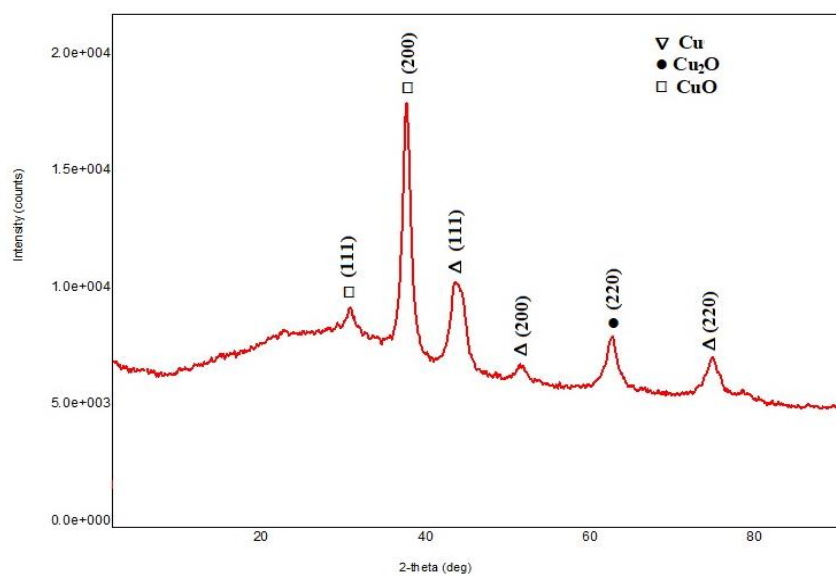
### 2.3. Characterization techniques

X-ray diffraction (XRD) analysis was performed with a diffractometer Rigaku Mini Flex 600 XRD (Cu  $K\alpha$  radiation  $\lambda = 1.54060 \text{ \AA}$ ; 30 kV and 15 mA) at room temperature. XRD patterns were collected in the range of  $2\theta = 10^\circ - 100^\circ$  with a step size of  $0.02^\circ$  scan and a time per step of 3 s. The morphology of the nanoparticles were determined by means of a scanning electron microscope model Jeol JSM-7600 F. Scanning was performed in second electron detecting (SEI) mode at an accelerating voltage of 15 kV and a working distance of 15.0 mm. Energy dispersive micro-X-ray analysis was performed using the device X-Max 50 (Oxford Instruments). Photoluminescent properties were examined using a spectrofluorimeter Varian Cary Eclipse at wavelength range 200-900 nm. Kinematic viscosity measurements were performed on a Stabinger SVM in ASTM D 445 mode. Density measurements were carried out in the ASTM D5002 mode on the DMA 4500 M device.

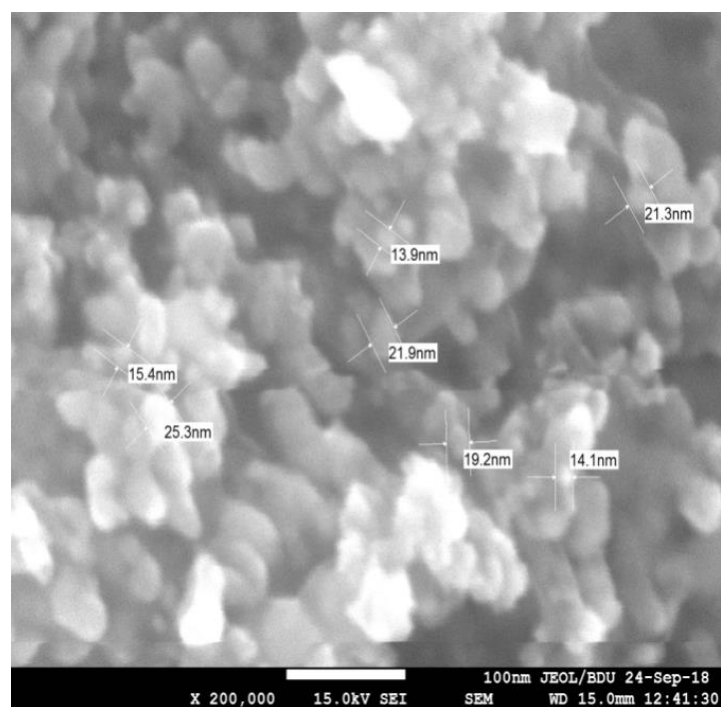
## 3. Results and Discussion

Figure 1 shows the XRD spectrum of copper nanoparticles obtained by the chemical reduction method. It was determined that the main peaks at  $42.94^\circ$  (111),  $50.49^\circ$  (200), and  $74.18^\circ$  (220) values of  $2\theta$  angle belong to copper nanoparticles with cubic structure, according to JCPDS No. 04-0836 base. It was also determined that there are maxima, belonging to copper oxide particles in the diffractograms. It is assumed that the synthesized nanoparticles are mainly copper in the core, and their surface is covered by a copper oxide layer (Nakamura *et al.*, 2007; Sun *et al.*, 2005; Wu *et al.*, 2004).

Figure 2 shows SEM image and EDS spectrum of copper nanoparticles. Figure 3 shows the elemental mapping of nanoparticles. The energy-dispersive spectrum and elemental mapping of the nanoparticles show a very small percentage of oxygen and a high amount of copper nanoparticles, which again indicates that the surface of the Cu nanoparticles is covered by a thin layer of copper oxide. From the SEM images, it was also determined that the average size of copper nanoparticles is 14-25 nm (Zhao *et al.*, 2004; Zhu *et al.*, 2004; 2005).



**Fig. 1.** XRD spectra of copper nanoparticles obtained by chemical reduction method



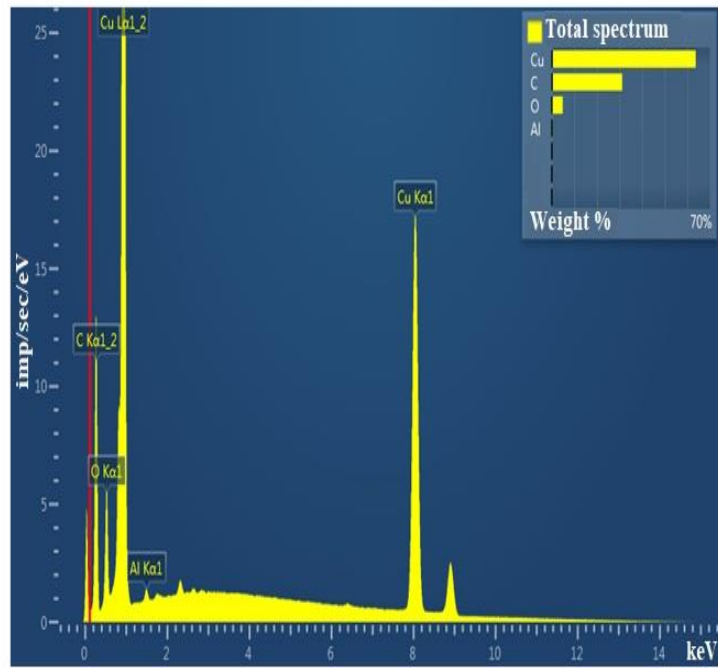
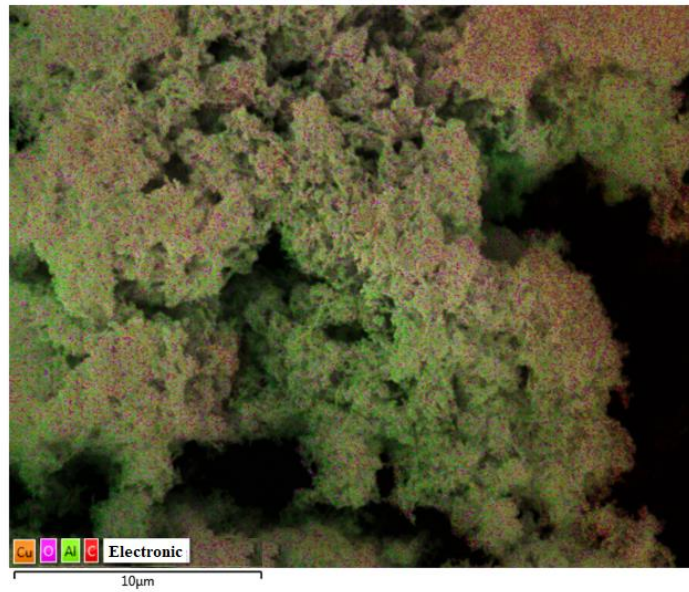
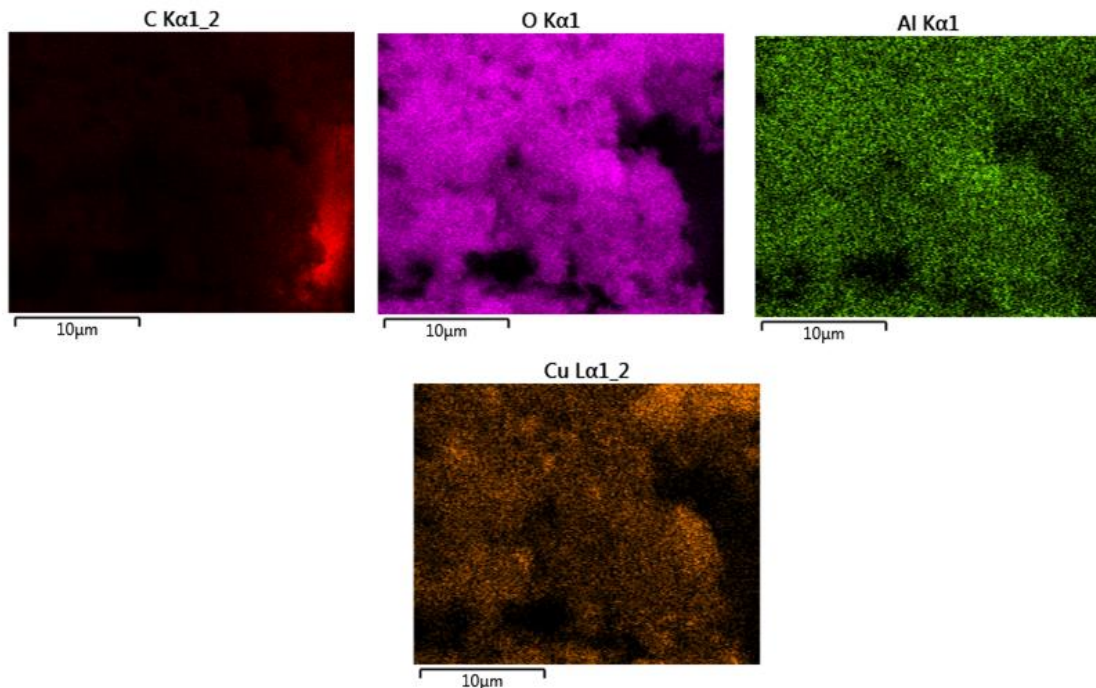


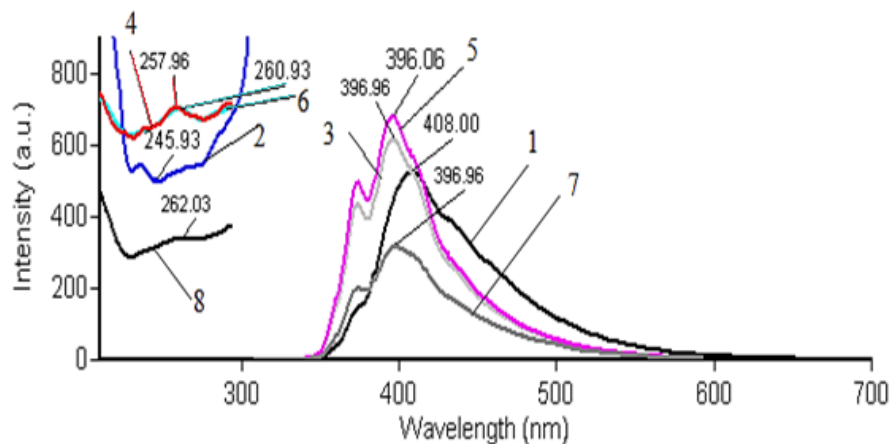
Fig. 2. SEM image and EDS spectrum of copper nanoparticles

Multilayered image EDS 16





**Fig. 3.** Mapping of nanoparticles sample by elements



**Fig. 4.** PL spectra of naftalan oil with copper nanoparticles

Figure 4 shows the effect of copper nanoparticles, obtained by chemical reduction method, on the photoluminescence properties of Naftalan oil. It was determined that the addition of small amounts of copper nanoparticles into the Naftalan oil leads to an increase of photoluminescence intensity of the oil. Furthermore, with the introduction of copper nanoparticles into Naftalan oil, the characteristic peak of Naftalan oil at 408 nm shifted to 396 nm. In addition, further increase in the amount of copper nanoparticles leads to a decrease in the photoluminescence intensity up to lower than that of raw Naftalan oil.

- 1) Em\_ex250nm\_naftalan
- 2) Ex\_408nm\_naftalan
- 3) Em\_ex250nm\_naftalan+0.005M Cu-CuO
- 4) Ex\_em396.96nm\_naftalan+0.005M Cu-CuO



- 5) Em\_ex250nm\_naftalan+0.01M Cu-CuO
- 6) Ex\_em396.96nm\_naftalan +0.01M Cu-CuO
- 7) Em\_ex250nm\_naftalan+0.05 M Cu-CuO
- 8) Ex\_em250nm\_naftalan+0.05 M Cu-CuO

Table 1 demonstrates the change in the physical properties of the oil of Naftalan oil with different fractions of copper nanoparticles.

**Table 1.** Physical properties of naftalan oil containing copper nanoparticles

Sample	Kinematic viscosity, mm <sup>2</sup> /sec, 20 °C	Density, g/sm <sup>3</sup>	Refractive index, 20 °C
Tar-free naftalen oil	32.194	0.9152	1.5030
Tar-free dearomatized naftalen oil	4.1484	0.8656	1.4721
Crude naftalan oil	63.485	0.9351	-
Tar-free naftalen oil+Cu-CuO nanoparticles	23.122	0.9038	1.3167
Tar-free dearomatized naftalen oil+Cu-CuO nanoparticles	4.1282	0.8612	1.5031
Crude naftalan oil+Cu-CuO nanoparticles	51.652	0.9335	-

As can be seen, the kinematic viscosity of partially dearomatized oil is much lower than tar-free oil, that is, the fluidity of partially dearomatized oil is higher. Unrefined crude Naftalan oil has quite high viscosity, and its kinematic viscosity value is much higher than that of unrefined and dearomatized Naftalan oil. It has been determined that the value of kinematic viscosity, density, and refractive index of oil decreases with the introduction of copper nanoparticles into crude, unrefined and dearomatized Naftalan oil. A decrease in kinematic viscosity indicates an increase in the fluidity of Naftalan oil. The decrease in the density of Naftalan oil by adding nanoparticles is an indicator of obtaining a lighter oil. After adding copper nanoparticles to tar-free Naftalan oil, the decrease in the refractive index of the oil is explained by the transition from the higher molecular fraction to the lower molecular fraction. The decrease in the refractive index of Naftalan oil after the introduction of metal oxide nanoparticles can also be explained by the decrease in the amount of naphthene and aromatic hydrocarbons in the oil, and the presence of saturated hydrocarbons in the oil. It is possible to explain the decrease in the amount of naphthene and aromatic hydrocarbons in naphthalene oil after the introduction of copper nanoparticles by the catalytic effect of small metal oxide nanoparticles.

The reduction of the viscosity of Naftalan oil by adding nanoparticles is an indicator of its fluidity, which opens up wider opportunities in the use of therapeutic Naftalan oil. Also, considering that CuO nanoparticles have antimicrobial properties, the inclusion of such nanoparticles in Naftalan oil will further expand its application possibilities.

#### 4. Conclusion

Have been synthesized and stabilized of copper nanoparticles by the chemical reduction method in the presence of sodium oleate as a surfactant. XRD, SEM, and EDS analysis showed that the surface of the nanoparticles is covered with a thin layer of the copper oxide film. The size of the synthesized and stabilized copper nanoparticles is 14–25 nm. After the introduction of copper nanoparticles, the photoluminescent properties of

various oil fractions have been studied. Have been established that the photoluminescence intensity of the oil increased as a result of adding small amounts of copper nanoparticles. The paper also revealed that the introduction of nanoparticles into oil leads to a decrease in the kinematic viscosity, density, and refractive index of oil.

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