Synthesis and Characterization of Nano-Strontium Oxide (SrO) Using Erzincan Cimin Grape (*Vitis vinifera*, Cimin)

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ABSTRACT

Aims: Synthesis of Strontium oxide (SrO) is very remarkable for its applications in electrodes for gas sensors, lithium-ion batteries, solar cells, doped dye-sensitive solar cells, transistors, catalyst supports, super capacitors and semiconductors. This study is intended to synthesize SrO nanoparticles using a new method because it has a wide application area as mentioned above.
Experimental design: Synthesis of SrO nanoparticles (NPs) was planned to be obtained by bio-reduction method using the plant extract of Erzincan Cimin grape (*Vitis vinifera*, Cimin)
Place and Duration of Study: The experimental steps of the study were carried out in the laboratories of Atatürk University, Erzurum Vocational College, Department of Chemical and Chemical Processing Technologies.
Methodology: In this study, the synthesis of SrO NPs was made by using aqueous extract of Erzincan Cimin grape (*Vitis vinifera*, Cimin). Biosynthesis medium containing 0.1 M $Sr(NO_3)_2$ was added to Cimin grape extract to synthesize SrO NPs.
Results: The structural characterization of the SrO NPs that were obtained as a result of the reaction was analyzed using SEM, EDAX and FTIR techniques. Using the X-ray diffraction pattern in the study, the mean particle size was calculated to be 28.6 nm. SEM analysis revealed that particles having a porous nanostructure in 20-50 nm of size were synthesized. It was determined that SrO nanoparticles were absorbed at 203 nm using UV spectrophotometer. At the end of the experiments, it was observed that the maximum synthesis rate was reached at 90 minutes, at 40^{o}C and at pH8.
Conclusion: The newly synthesized nanomaterial is expected to find applications in many different areas thanks to its physical and chemical properties.

Key Words: *Erzincan Cimin Grape (Vitis Vinifera, Cimin), Strontium oxide NP, Green synthesis*

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1. INTRODUCTION

The developments in the synthesis approaches of nanomaterials are distinguished by the acquisition of new chemical and physical properties. Today, with the use of green synthesis reactions, it has gained significant momentum in the synthesis of many metal oxide nanoparticles. The synthesis of nanoparticles from oxides of transition metals such as strontium oxide (SrO) is significant due to the structural diversity and wide range of applications. SrO NPs have long been investigated for their promising applications in manufacture of gas sensors, lithium-ion batteries, solar cells, doped dye-sensitive solar cells, transistors, catalyst supports, supercapacitors and electrodes for semiconductors[1-5]. Some studies reported the sol-gel synthesis method of SrO NPs and investigated the optical and thermal properties of nanoparticles. In another study, Nemade and Waghuley reported that they produced strontium oxide nanoparticles using a one-step chemical precipitation method [6]. In all known synthetic methods, extreme conditions (high temperature, organic solvents, high-precision precursors, toxic reducing agents, and special atmospheric media) are used and there are many disadvantages such as requiring a few steps to perform an experiment. In addition, many of the chemical reducing agents and solvents used in these methods carry biological risk and are harmful to the environment. There is very little literature on the synthesis of SrO NPs in currently used methods, and these methods have their own limitations.

To overcome this disadvantage, many researchers nowadays use various plant (or herbal) extract, such as Pomegranate (*Punica granatum*), Basil (Ocimum sanctum), Papaya (Carica papaya) and Cabbage (Brassica oleracea) to synthesize nanoparticules. A great interest has been shown for the development of novel and simple approaches to nanoparticle synthesis that use plant compounds as reducing agents. Diverse morphology and nanoscale size have a crucial impact on improved physical and electrical properties of synthesized nanoparticles. In addition, under moderate conditions, green chemical synthesis pathway for the preparation of SrO NPs has distinguished with a moderate approach such as room temperature and neutral pH. Researchers have begun to find and develop new, economic and environmentally friendly methods for reasons such as environmental pollution factors and cost increase in the synthesis of nanoparticles.

Therefore, Erzincan Cimin grapes (*Vitis vinifera*, Cimin) were used as reducing agents in the synthesis of SrO NPs. It is a variety of black grape grown in Erzincan province, Turkey. In the past, the grape and its products were known good among the public for treatment of diseases. Today, Erzincan Cimin grapes are known to be used in food and health sector [7]. It is considered that grape extract may be used as a reducing and stabilizing agent in green nanosynthesis thanks to the presence of important components such as sugar derivatives, alkaloids and terpenoids [8,9]. Investigations showed that there are no other research that uses Erzincan Cimin grape in synthesis of SrO NPs. Therefore, SrO NPs were aimed to be synthesized and characterized in more efficient, economical and moderate conditions using Cimin grape.

2. MATERIAL AND METHODS

2.1. Chemical and reagents

An endemic species of Cimin grape (*Vitisvinifera cv.* Cimin) was obtained from Erzincan province in September 2017. $Sr(NO_3)_2$, Sodium acetate ($NaCH_3COO$), Tris ($(HOCH_2)_3CNH_2$), Sodium carbonate (Na_2CO_3), Sodium hydroxide (NaOH), Hydrochloric acid (HCl) were purchased from Sigma-Aldrich GmbH, (Sternhe I Germany). The other chemicals were obtained from Merck. All solutions were prepared using deionized water. All the materials to be included in the experiments were disinfected in the oven and sterilized to ensure a clean environment.

Comment [FM1]: Purity???

2.2 Preparation of the reaction medium;

The Cimin grapes (*Vitisvinifera cv.* Cimin) obtained from Erzincan were washed with pure water. They were then rinsed, dried and stored in a freezer at -20 °C untilthey were employed. An aqueous extract of grapes was prepared, and used in the green synthesis reaction medium. In a simple procedure, 100 grams of Cimin grape (*Vitisvinifera cv.* Cimin) was blended with 250 mL of pure water for 30 minutes at 300 rpm until a homogeneous mixture is obtained. The homogenate was then filtered through a filter paper, then the filtrate was centrifuged at 3000 xg to remove heterogeneous moieties. The resulting Cimin grape (*Vitisvinifera cv.* Cimin) aqueous extract was used as the reaction medium for synthesis [10,11].

Comment [FM2]: Deionized?

2.3. Green synthesis of SrO NPs;

The prepared 50 mL grape extract was added carefully to the solution prepared with the water-soluble salt of 0.1 M Sr metal (500 mL) (Figure 1). The green synthesis reaction was monitored by spectrophotometer for 72 hours under normal atmospheric pressure and room conditions with stirring at 300 rpm. The conversion of Sr metal in the reaction medium to SrO NPs was monitored at 200-1000 nm using a spectrophotometer and the wavelength of the SrO NPs was determined to be 203 nm [6]. This determined wavelength was used in the next optimization process. The effects of time, pH, temperature and metal ion concentration parameters on nanoparticle synthesis were determined separately for optimization [6].

Comment [FM3]: UV-Vis spectrophotometry

Comment [FM4]: under

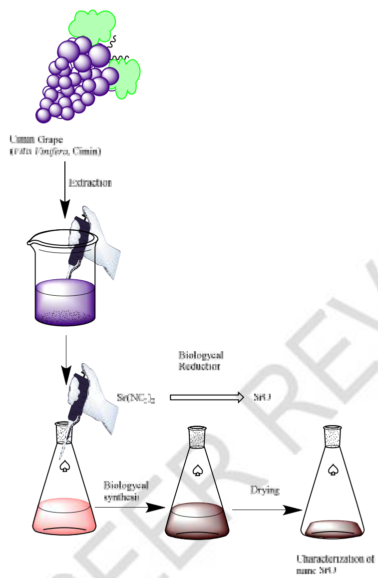


Figure 1. Synthesis of Nano Strontium Oxide (SrO) from Erzincan Cimin Grape (*Vitis vinifera,* Cimin)

2.3.1. Interaction time

Samples from the reaction medium prepared with $Sr(NO)_3$ was taken with a 3-minute interval and the spectrophotometer was monitored during the total reaction time of 240 minutes by measuring the absorbance (203 nm) against the blank solution, and the time of formation of the SrO NPs was determined at its highest.

2.3.2. Optimum pH

The most efficient pH for the synthesis of SrO NPs was investigated by using different buffer solutions. For this purpose, synthesis reaction media of SrO NPs were prepared using phosphate buffer for reaction media of pH: 2-3, pH: 4-6, and pH 7-8, and carbonate buffer for pH: 9-11. The formation of SrO NPs and the changes in absorbance at 203 nm were monitored through UV-Vis spectrophotometer.

2.3.3. Optimum temperature

In order to determine the temperature at which the SrO NPs were synthesized more effectively, the reactions were carried out separately at temperatures between 10-90 °C (at intervals of 10 ± 2 ^{o}C). All measurements were made to keep the pH and metal ion concentration constant so that the only variable was the temperature of the reaction medium. All measurements were made UV-Vis spectrophotometrically against the blank sample.

2.3.4. Optimum Metal Ion Concentration

Different concentrations of solutions (0.05M, 0.1M, 3M, 5M and 7M) were prepared for the synthesis of SrO NPs. All measurements were made to keep the pH and temperature constant so that the only variable was the metal ion concentrations of the reaction medium. The effect of metal ion concentration on the nanoparticle synthesis reaction was determined spectrophotometrically (at 203 nm).

After all conditions were optimized, the obtained SrO NPs were collected, dried and then characterized.

2.4. Characterization of SrO NPs

The synthesized SrO nanoparticles were characterized by a UV-VIS spectrophotometer (Epoch Nanodrop UV-VIS spectrophotometer), scanning in the 200-1000 nm range. The topographic analysis of SrO nanoparticles was performed by SEM (Scanning Electron Microscope) analysis. The ratios of structural components of SrO NPs were determined by EDAX chromatography. By FTIR chromatography, the interactions of the organic excess SrO NPs will be determined and structural characterization of the synthesized NP will be made [12,13].

Comment [FM5]: Microscopy

Comment [FM6]: EDAX is NOT a chromatographic technique!!!!!

Comment [FM7]: FTIR is NOT a chromatographic technique!!!!!

3. RESULTS AND DISCUSSION

Strontium is a compound having thermal, electrical and electro catalytic activity. It is also used in dentistry and dental applications[1]. Strontium (Sr) has been reported to be one of the important trace elements that strengthen bones in the human body and prevent caries[14]. In previous studies for the synthesis of SrO NPs, various chemical and physical methods have been employed, such as sol-gel, co-precipitation, hydrothermal and spray pyrolysis. Conventional hydrothermal methods have also been used for the synthesis of SrO nanoparticles. In particular, by means of microwave hydrothermal synthesis, high temperature heat treatment which can lead to particle growth and agglomeration can be avoided. However, the use of large amounts of strontium precursors and low yield are two major disadvantages of the current methods [15]. In another study, it has been reported that Strontium oxide (SrO) NPs are synthesized by hydrolysis of single source molecular precursor SrCl2•6H2O with potassium hydroxide whereafter the structure, morphology and properties of the particles were characterized using XRD, TEM, Raman and UV-VIS spectroscopic tecniques [15].

In this study, using Cimin grape extract, SrO NPs were synthesized in high efficiency and moderate conditions. The size and purity of the nanoparticle were improved by optimizing the synthesis curves (pH, temperature, reaction time, etc.). The reactions were carried out at 203 nm using an UV spectrophotometer. At the end of the experiments, for optimization of the method, it was determined that the SrO NPs at 0.1 M metal ion concentration, 40 ^oC, pH 8, reached the maximum synthesis rate in 90 minutes.

Comment [FM8]: Reactions at 203 nm??? Please, explain!

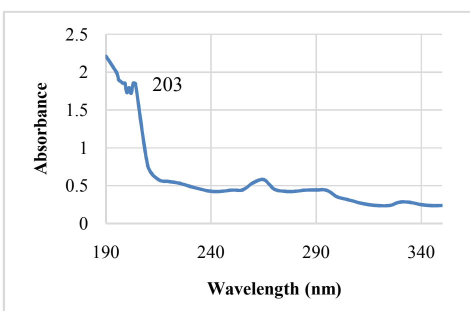


Figure 2. Spectrophotometric wavelength scanning of SrO NPs

After optimizing the reaction, the characterization of the obtained nanoparticles was performed. Figure 3 shows the SEM image of the SrO NPs obtained from the SEM analysis. It was understood from SEM image (Figure 3) that the shape of the SrO NPs is in a nearly spherical arrangement on a smooth surface, which bound together parallel, as small layer formation with a diameter range of 20–50±2.5 nm.

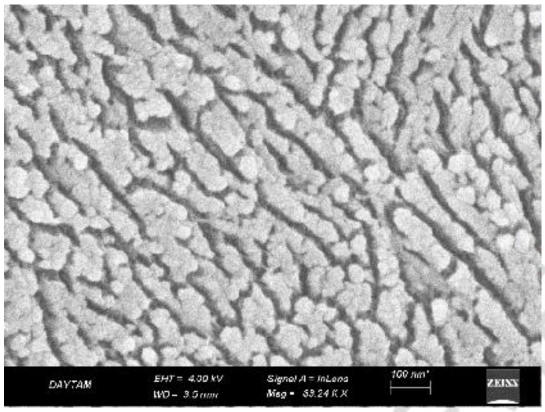


Figure 3. SEM image of SrO NPs

In Figure 4 is EDAX analysis of SrO nanoparticles. Based on data from EDAX analysis and SEM chromatography results support the formation of SrO nanoparticles.

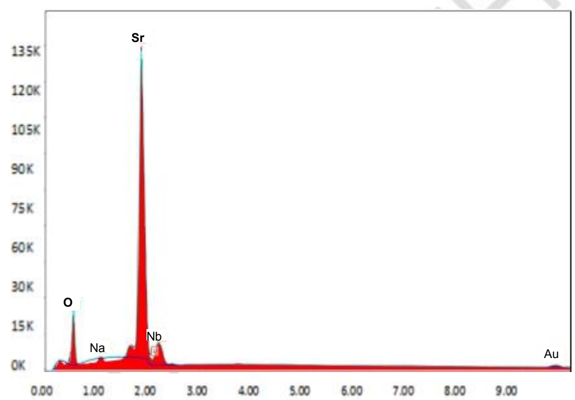


Figure 4. EDAX analysis result

FT-IR chromatography technique was used to obtain information about the binding of SrO NPs with the organic phase. In detail, the absorption bands at 3664.35 cm^{-1} originates from stretching vibration and deformation vibration of O-H. The strong broad absorption peak at about 1473.81 cm^{-1} is attributed to the asymmetric stretching vibration of Sr-O, the sharp absorption bands at 956.59 cm^{-1} and 885.23 cm^{-1} can be attributed to out-of-plane bending vibration of Sr-O. The two bands at 1255.52 cm-1 are attributed to the C-O vibrations. [16-18]. The sharp absorption bands at 1083.87 cm^{-1}, 1317.72 cm^{-1}, 1473.81 cm^{-1}, 1610.38 cm^{-1}, 2979.70 and 3276.70 cm^{-1} can be attributed to bending vibration of O-H and stretching vibrations of C-O[15]. The presence of C-O, O-H, C-C, and C-N peaks indicates that all SrO NPs are

Comment [FM9]: ¿?

Comment [FM10]: Sure?

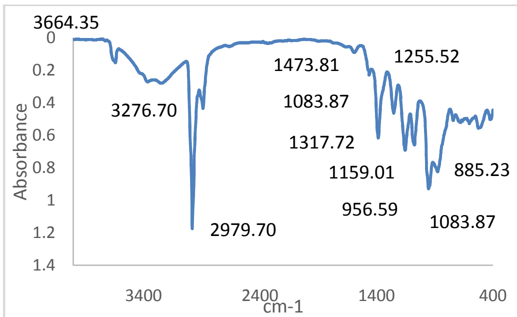
Comment [FM11]: SEM chromatography????? Do the authors know what they are talking about?

Comment [FM12]: Again...FTIR is NOT a chromatographic technique!!!!!

Comment [FM13]:

Comment [FM14]: Are you sure that the instrument used provides this accuracy?

formed using the Cimin grape extract as reducing agent and also Cimin grape is acting as capping agent on the surface of metal oxide nanoparticles (Figure 5).



Comment [FM15]: Indicate which peak corresponds to each numerical value

Figure 5. FTIR spectrum of SrO nanoparticles

4. CONCLUSION

So far, various chemical methods are known for synthesis of SrO NPs, such as sol-gel, co-precipitation, hydrothermal and spray pyrolysis. Today, due to cost-reducing and environmentally friendly approaches, the use of green chemical reactions has gained significant momentum in the synthesis of NPs from a large number of metal oxides. For this reason, the synthesis of SrO nanoparticles having a widespread use is an important and interesting research topic. According to the results obtained from SEM, XRD and FTIR analyses, nano-sized strontium oxide particles can be synthesized by the method used in this study. It is concluded that these synthesized nanoparticles can be used because of the advantages they gained with this production approach in many industrial areas.

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