Characterization of Cr₂O₃ Nanoparticles Prepared Using Cauliflower Extract by Two Methods

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Abstract
Chromium oxide nanoparticles were synthesized using cauliflower extract by two methods: simple chemical method and the sol-gel method. These technologies are new, environmentally friendly and cheap. Cauliflower contains plant materials and biomolecules (chromium, phenols, alkalis, vitamins, amino acids, quinones, etc.) that convert chromium chloride hexahydrate (CrCl₃·6H₂O) into chromium nanoparticles. The plant extracts also act as diluents, stabilizers and anti-caking agents. X-ray diffraction (XRD) analysis showed that the size of the crystals decreased from (36.1 to 57.8) nm using the simple chemical method to (13.31 to 20.68) nm of Cr₂O₃ using sol-gel. The scanning electron microscopy (SEM) showed that Cr₂O₃ NPs of the simple chemical method were Nano layers with (130.3) nm, while the Cr₂O₃ NPs of the sol-gel method were spherical or semispherical in shape with a particle size of (14.89 to 39.08) nm. The results obtained have no matches in the reported literature. Ultraviolet-visible (UV-Vis) showed that the band gap energy of Cr₂O₃ NPs of the simple chemical method was 2.5 eV, while it was 3.4 eV for Cr₂O₃ NPs of the sol-gel method. Cr₂O₃ NPs of high purity, small particle size, and large energy gap were obtained from the sol-gel method. This means that the NPs from the sol-gel method were better than those of the simple chemical method. The study revealed that the Chromium oxide nanoparticles synthesized using cauliflower extracts could be used as antibacterial agent for human pathogenic bacteria.

Keywords: Cr₂O₃ NPs, plant extracts, green chemistry, Antimicrobial activity
1. Introduction

The study of fine and ultrafine particles has received increasing interest due to the new properties that the material may show when the grain size is reduced [1]. During the past decades, considerable progress in the synthesis of nano-particles has been achieved. Nanomaterials, particularly transition-metal oxides play an important role in many areas of chemistry, physics and material science [2]. Nanotechnology is one of the most active areas of research in modern materials science; nanotechnology has become a form of the pioneering and exciting field in chemistry, physics, and biology. The study of nanoparticles has received increasing attention due to the material's novel qualities that may emerge as particle size is lowered. Nanotechnology can describe the fabrication and characterization of nanomaterials, (1-100) nanometers, for the development of science [2]. Nanotechnology is an enormously powerful technology, which holds a huge promise for the design and development of many types of novel products with its potential medical applications on early disease detection, treatment, and prevention. Nanoparticles are shown new (improved) properties based on specific characteristics such as size, distribution, and morphology [3]. The nanoscale dimension is important because quantum mechanical properties of electronics, photons and atoms are shown at this scale. In addition, nanostructures allow controlling the correction of materials without changing the chemical state. In general, nanotechnology plays an important role in the specialized qualities of the most innovative scientific field. Nanotechnology. It is mainly involved in the manufacture of nuclear plants in various sizes, shapes, chemical compositions, chemical compositions [4,5]. The major benefits of NPs over larger particles are high surface-to-image ratio. In the last two decades, nanostructured materials have undergone extensive study due to their unique specialization and applications in the many fields [6]. Nanotechnologies involved in the fabrication of nano materials may be classified as top-down or bottom-up approaches. Top-down (physical methods) or bottom-up (chemical and biological methods) is a measure of the level of advancement of nanotechnology. The NPs which can be synthesized by both top-down (physical) and bottom-up (chemical methods and via a green pathway as in this research) [7]. In technological applications, conventional metal oxides are used in the manufacture of electronic circuits, motorcycles, fuel cells, and coatings to protect the surface from corrosion, and as a catalyst [8]. The development of nanomaterials has garnered great interest, especially in the physical, chemical and biological sciences for their performance in the manufacture of microelectronics, transistors, and light emitting diodes as well as in cancer treatment [9].

2. Experimental

2.1 Materials

All the chemicals used were of highest purity available and were used as received without further purification or distillation: [CrCl\(_3\).6H\(_2\)O] (99.5%, Sigma-Aldrich), sodium hydroxide (NaOH) (99%, Fluka), cauliflower extract; its source was from local market.
2.2 Preparation of Plant extracts

In a simple chemical method, small parts of the cauliflower plant were purified from impurities, and cut into small pieces and left in the sun for two days. After that it was grounded to fine powder with a solid metal electric mixer. The plant extracts were made from a mixture of 5 g of powder in 100 ml of deionized water. The solution was heated at 70 °C for 30 min on a magnetic stirrer. The resulting aqueous solution was cooled at room temperature and purified during Whitman’s filtration Figure 1 an explanation of the steps for converting a fresh plant into an extract. In the sol - gel method.

2.2.1 Preparation of chromium oxide NPs by the simple chemical method

Non-synthesized Cr₂O₃ NPs (50 mL, 1 M) and chromium chloride hexahydrate (CrCl₃.6H₂O) were added to 100 mL of the prepared cauliflower extract. This prepared solution was placed on a magnetic stirrer at 70 °C for 30 min. After that, the solution was left to cool to room temperature. 25 mL of Cr₂O₃ was placed in a ceramic oven at 200 °C for two hours to obtain a nano-base. The Cr₂O₃ NPs powder was stored in sealed labeling serum tubes. Figure 2 shows the stages to prepare NPs using cauliflower extracts.

Figure 1 - Stages of converting fresh plant into extract (cauliflower), A) Plant, B) powder, C) extract.

Figure 2 - The stages of preparation of chromium oxide NPs (A) chromium chloride hexahydrate (CrCl₃.6H₂O) solution, (B) cauliflower extract, (C) Cr₂O₃ solution, (D) Cr₂O₃ NPs powders.
2.2.2 Preparation of chromium oxide NPs by the sol-gel method

5 grams of (Cauliflower) powder was used in 100 ml of distilled water and putted on the magnetic stirrer for two hours at 70 °C, 13 grams of chromium sulfate is taken with 50 ml of distilled water for 10 minutes on the magnetic stirrer and then filtered using filter paper and then after filtering, a centrifuge is used at 15,000 cycles for 10 minutes. Then, CrCl₃ is added over the plant extract for half an hour on the magnetic stirrer, and then it is placed on to turn it into a gel. After that, and place on the magnetic stirrer. Then several drops of sodium hydroxide were add to the solution until it attained pH = 7. The temperature was increased to 90°C and left to turn into liquid (Gel). Thus it was allowed to stay for one and the half hour after which the temperature was increased to (120°C) and left to become dry gel (Xerogel) , then lifted and left to cool down. The powder was collected and placed in a container of porcelain and inserted into the oven 25 ml of the solution is taken and placed in a ceramic eyelid and placed in an oven at (200)°C for two hours. After turning off the oven, the sample is left inside for 24 hours to obtain a Nano powder.

Figure 3-explains of fresh chromium oxide NPs using cauliflower extract (A) a simple chemical method, and (B) in the sol-gel method

3. Results and Discussions
3.1 X-ray Diffraction (XRD) of chromium oxide NPs prepared by the simple chemical method.

XRD is an important technique that is commonly used to investigate the structural properties to ascertain the crystalline nature and phase identification of chromium oxide nanocrystalline films. From Figure 4, it is noticed that the 012 and 104 peaks are the preferred orientations of prepared (Cr₂O₃) NPs using cauliflower plant. Table (1) shows the XRD results of Cr₂O₃ NPs. The crystallite size (D) was estimated by the following Scherrer’s Equation (1).
Where \( k \) is called shape factor (0.9), \( \lambda \) is the wavelength (0.15418), \( \beta \) is full width at half maximum (FWHM), and \( \theta \) is a diffraction angle.

\[
D(\text{nm}) = \frac{K\lambda}{\beta\cos\theta}
\]  

(1)

**Figure 4**-XRD pattern of Cr\(_2\)O\(_3\) NPs prepared by the simple chemical method using cauliflower extract.

**Table 1**-XRD results of Cr\(_2\)O\(_3\) NPs prepared by the simple chemical method using cauliflower extract.

| Plant Extract | Material | FWHM (deg.) | 20 Exp. (deg.) | (hkl)  | 20 JCPDS (deg.) | Crystallite size D (nm) |
|---------------|----------|-------------|----------------|--------|----------------|------------------------|
| cauliflower   | Cr\(_2\)O\(_3\) | 0.14        | 25.7           | (012)  | 25.1           | 57.8188888818           |
|               |          | 0.22        | 33.8           | (104)  | 33             | 36.1                   |

3.2 X-ray Diffraction XRD for chromium oxide NPs by the sol-gel method.

It is noticed from Figure 5 that the peaks (012), (104), (110), (202) and (122) are the preferred orientation of Cr\(_2\)O\(_3\) NPs.
Figure 5-XRD Patterns of Cr$_2$O$_3$ nanoparticles prepared by the sol-gel method using cauliflower extract.

Table 2-XRD results of Cr$_2$O$_3$ nanoparticles prepared by the sol-gel method using cauliflower extract.

| Plant Extract | Material | FWHM (deg.) | 20 Exp. (deg.) | (hkl) | 20 JCPDS (deg.) | Crystallite Size D(nm) |
|---------------|----------|-------------|----------------|-------|-----------------|-----------------------|
| cauliflower   | Cr$_2$O$_3$ | 0.393       | 23.51          | (012) | 23.1            | 20.68                 |
|               |          | 0.49        | 33.82          | (104) | 33.2            | 16.14                 |
|               |          | 0.59        | 37.86          | (110) | 37.5            | 13.31                 |
|               |          | 0.49        | 46.4           | (202) | 45.5            | 15.5                  |
|               |          | 0.36        | 58.75          | (122) | 59.2            | 20                    |

Figure 4-1- XRD patterns of Cr2O3 NPs (JCPD) Card no. 96-210-4123[10].

3.3 Scanning Electron Microscopy (SEM) of chromium oxide NPs prepared by the simple chemical method at 200 °C.
SEM image measurements were performed to determine the surface morphology of chromium oxide NPs using cauliflower extract prepared by the simple chemical method. Figure 6 (A-D) shows the shape and average size of Cr$_2$O$_3$ NPs. It is seen as e (Nano layers).

![Figure 6 SEM analysis of Cr$_2$O$_3$ NPs prepared by the simple chemical method using cauliflower extract at 200°C.](image)

3.4 Scanning Electron Microscopy (SEM) of chromium oxide NPs prepared by the sol-gel method at 200°C.

Figure 7 (A-D) are the SEM images of the (Cr$_2$O$_3$) NPs prepared by the sol-gel method using cauliflower extract. It shows that the nanoparticles are spherical or semispherical in shape with a particle size of (14.89 to 39.08) nm.

![Figure 7 SEM analysis of Cr$_2$O$_3$ NPs prepared by the sol-gel method using cauliflower extract at 200°C.](image)

3.5 UV-Vis properties of chromium oxide NPs prepared by the simple chemical method

The samples were examined by UV-Vis spectroscopy to determine the absorbance of the Cr$_2$O$_3$ NPs cauliflower extract. Figure 8 shows the optical transmittance spectra of (Cr$_2$O$_3$) NPs prepared by the simple chemical method (as shown in Figure 8. The spectrum, at the spectral range of (200-900) nm, shows a low transmittance at 400 nm resulting in strong absorption of (Cr$_2$O$_3$) in this region.

The energy gap of the (Cr$_2$O$_3$) NPs was estimated by plotting $(a h\nu)^2$ against the photon energy $(h\nu)$. The intercept of the extrapolation of the linear part of the graph with the $h\nu$ axis
gives the energy gap value. The gap depends on the energy band, the crystal structure of the film and the arrangement and distribution of the atoms in the crystal lattice. The optical band gap value of (Cr$_2$O$_3$)NPs was 2.5 V as shown in Figure 9.

**Figure 8**-UV-Vis transmission spectra of Cr$_2$O$_3$ NPs prepared by the simple chemical method using cauliflower extract.

**Figure 9**-Energy band gap of Cr$_2$O$_3$ NPs prepared by the simple chemical method using cauliflower extract.
3.6 UV-Vis properties of chromium oxide NPs prepared by the sol-gel method.

Figure 10 shows a high transmittance percentage above 400 nm indicating the strong absorbance of Cr₂O₃ in this region. All films showed increase in transmittance at the wavelengths longer than 400 nm.

The optical band gap of chromium oxide NPs was calculated by plotting \((\alpha h\nu)^2\) versus \(h\nu\) and by extrapolating the straight line of the curve to the \(h\nu = 0\) as shown in Figure 11. It was found that the Cr₂O₃ NPs have direct transition type and the bandgap has increased from 2.5 eV to 3.4 eV with the sol-gel method. Increase of the optical energy gap of chromium NPs with the sol-gel method can be ascribed to the formation of smaller chromium oxide NPs.

Figure 10-UV-Vis transmission spectra of Cr₂O₃ NPs prepared by the sol-gel method using cauliflower extract.

Figure 11-Energy band gap of Cr₂O₃ NPs prepared by the sol-gel method using cauliflower extract.
3.7 Comparison between chromium oxide NPs prepared by the simple chemical method and the sol-gel method.

It was noted that chromium oxide NPs prepared by the simple chemical method were less pure and were not completely good, but when the result using the sol-gel method was excellent. An increase in purity, a decrease in the particles size and an increase in the energy gap were noted. Table (3) shows the results of chromium oxide NPs from the two methods.

**Table 3-** The results of chromium oxide NPs in two methods

| Plant Extract | Material in a simple chemical method | Crystallite size D(nm) | Particle size (nm) | Energy gap (ev) |
|---------------|--------------------------------------|------------------------|--------------------|-----------------|
| cauliflower   |                                       | 36.1                   | 130.3              | 2.5             |
|               |                                       | 57.8                   |                    |                 |
|               | In a sol-gel method                   | Crystallite size D(nm) | Particle size (nm) | Energy gap (ev) |
|               |                                       | 20.68                  | 14.89              | 3.4             |
|               |                                       | 16.14                  |                    |                 |
|               |                                       | 15.5                   | 39.08              |                 |
|               |                                       | 20                     |                    |                 |

Antibacterial Activity of Cr$_2$O$_3$ NPs
The antimicrobial activity of Cr$_2$O$_3$ NPs synthesize have been examined against bacterial cultures Gram-positive (Bacillus subtilis), Gram-negative (Escherichia coli), and against fungal cultures (Candida albicans) using agar well diffusion method[11].

**Table 4-** The antibacterial activity of the Chromium oxide nanoparticles prepared using cauliflower extract against the tested bacteria as demonstrated by diameters of the inhibition zone (mm)*

| Isolated bacteria   | Cr$_2$O$_3$ nanoparticles synthesized by | Inhibition zone |
|---------------------|-----------------------------------------|-----------------|
|                     | Cauliflower extract (simple chemical method) | 21              | 16              |
| Staphylococcus aureus + | Recreation of coding | 22              | 20              |
| Staphylococcus epidermidies + | Recreation of coding | 22              | 19              |
| Escherichia coli - | Recreation of coding | 21              | 17              |
| Klebsiella up - | Recreation of coding | 18              | 16              |
| Candida albicans | Recreation of coding | 18              | 16              |
The study using the cauliflower extract by the simple chemical and sol-gel methods. This work succeeded in converting CrCl\textsubscript{3}\cdot6H\textsubscript{2}O into chromium oxide nanoparticles. Also, the cauliflower extract acted as a reducing, stabilizing and anti-agglomeration agent. It was noted that the results of the sol-gel method are better than those of the simple chemical method. This was noticed by an increase in purity, a decrease in the size of particles and an increase in the energy gap. The prepared powders were characterized using XRD, SEM, and UV-Visible spectroscopy. No similar results were found in the literature on chromium oxide nanoparticles prepared using cauliflower extract. The study also revealed that chromium oxide nanoparticles prepared using cauliflower extract could be an antibacterial agent for human pathogenic bacteria.

### 4. Conclusion

This work succeeded in the biosynthesis of chromium oxide nanoparticles using cauliflower extract by the simple chemical and sol-gel methods. The cauliflower extract has succeeded in converting CrCl\textsubscript{3}\cdot6H\textsubscript{2}O into chromium oxide nanoparticles. Also, the cauliflower extract acted as a reducing, stabilizing and anti-agglomeration agent. It was noted that the results of the sol-gel method are better than those of the simple chemical method. This was noticed by an increase in purity, a decrease in the size of particles and an increase in the energy gap. The prepared powders were characterized using XRD, SEM, and UV-Visible spectroscopy. No similar results were found in the literature on chromium oxide nanoparticles prepared using cauliflower extract. The study also revealed that chromium oxide nanoparticles prepared using cauliflower extract could be an antibacterial agent for human pathogenic bacteria.

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