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Biofabrication of highly pure copper oxide nanoparticles using wheat seed extract and their catalytic activity: A mechanistic approach

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Abstract: A facile novel green methodology is presented for the synthesis of highly stable and well-dispersed copper oxide nanoparticles using aqueous wheat seed extract. Under optimal reaction conditions, the wheat seed extract-derived electron-rich biomolecules were functioned as a reducing and capping/stabilizing agent. The ultraviolet-visible absorption peak at 300 nm was confirmed the formation of copper oxide nanoparticles. Fourier-transform infrared spectroscopy analysis determined Cu–O bonds in nanosample, indicating the active role of functional groups in the wheat seed extract in bioreduction of Cu cations. X-ray diffraction pattern results demonstrated the monoclinic structure of highly pure biosynthesized copper oxide nanoparticles with a crystallite size of 20.76 nm. The stability of copper oxide nanoparticles was confirmed after 3 months' storage of product with no sedimentation or suspension. Transmission electron microscopy results showed the spherical shape of nanoparticle with an average size of 22 ± 1.5 nm. X-ray photoelectron spectroscopy analyses revealed only copper and oxygen elements in the sample, confirming the purity of copper oxide nanoparticles. Bio-assisted copper oxide nanoparticles demonstrated significant catalytic efficiency and reusability toward 4-nitrophenol removal by an average of 97.6% from aqueous solutions after successive 5 days' exposure to UV irradiation.

Keywords: copper oxide nanoparticle; wheat seed extract; biosynthesis; 4-nitrophenol removal; formation mechanism

Abbreviations

CuO	Copper Oxide
FTIR	Fourier-transform infrared spectroscopy
NPs	Nanoparticles
4-NP	4-Nitrophenol
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
T.	Triticum
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Powder Diffraction
UV-Vis	Visible and Ultraviolet Spectroscopy

1 Introduction

Nanoparticles owing to high surface area and a tiny particle size show inimitable material characteristics in comparison with bulk materials, which make them high in demand and widely applied area for miscellaneous applications in recent years. Presently, a considerable number of physical and chemical procedures were presented to fabricate the various types of nanoscale particles with different shape and size. Despite their popularity, they are high cost and often contain toxic materials (e.g. solvent, the reducing agent, acid and base reagents) which potentially expose the environment to serious health hazards; so that restricts their advantages. Whereas biological procedures are non-toxic, high atom economy, straightforward methodology and most importantly they are environment-friendly [1]. Hence, recent researches have been attempted to employ nature-based sources such as plants extracts [2,3], fungi [4], bacteria [5], and marine organisms [6], as sustainable alternative methods toward green nanoparticles fabrication [7]. Owing to presence highly active bio-organic molecules in plants, eco-friendly plant-based methodologies such as roots, flowers, seeds, leaves, bark, and fruits, have emerged as extremely promising biological factories for the formation of the diverse range of inorganic

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nanoparticles [8]. Apparently, their active biomolecules most likely comprise amino, hydroxyl, and carboxyl biofunctional groups which would function a dual role as a reductant of metal salts and as protective agents to form a stabilizing layer on the biosynthesized nanoparticles [9].

Copper oxide nanoparticles (CuO NPs) and their derivatives as a type of metal oxide nanoparticles due to fair stability, cost-effectiveness and readily available compared to other expensive noble metals like Au, Pt, and Ag are broadly used in many applications such as a colorant in many ceramics applications, including the preparation of slips and glazes [10], batteries, catalyst for chemical reactions [11], solar cell [12], chemical sensor [13,14], absorbent [15], thermal conductivity enhancer [16], antifouling properties [17], wastewater treatment [18,19], thermal conductivity and anti-oxidation properties [20], bio-control agent [21], drug delivery [22], anticancer activity [23], and efficient anti-microbacterial agent [24,25].

There are a wide variety of traditional chemical and physical methods for CuO NPs fabrication including electrochemical methods [26], sonochemical [27], alcohothermal [28], hydrothermal decomposition [29], precipitation [30], polyol [31], and gamma radiation [32]. To avoid serious environmental hazards and health effects of chemical synthesis methods, several reports on phyto-assisted synthesis of CuO NPs by different parts of plant extracts have been published including *abutilon indicum* leaf [33], *Saraca indica* leaves [34], *Rheum palmatum L.* root [35], *Aglaia elaeagnoidea* flower [36], *Malus domestica* leaf [37], and green pea [38].

Common wheat (*Triticum aestivum*), bread wheat, is an annual cereal grain cultivated in greater quantities for its seed. It considers a global staple food with the highest monetary yield [39]. Wheat is the major source of carbohydrate biomolecules such as starch and simple electron-rich reducing sugars (e.g. glucose, and fructose) [40]. Therefore, the goal of this study is to present an alternative new abundant natural source based on 12 principles of green chemistry for the rapid one-step fabrication of highly pure and safer CuO NPs by aqueous extract of wheat seed. Size, purity, shape and surface chemistry of as-prepared CuO NPs were scrutinized through Visible and Ultraviolet spectroscopy (UV-Vis), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM).

2 Experimental

2.1 Materials

Copper (II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) was acquired from Sigma-Aldrich supplier (USA) and utilized without further purification. Deionized (DI) water was used in all experiment steps for making molar solutions, washing, and dilution.

2.2 Preparation of the aqueous wheat seed extract

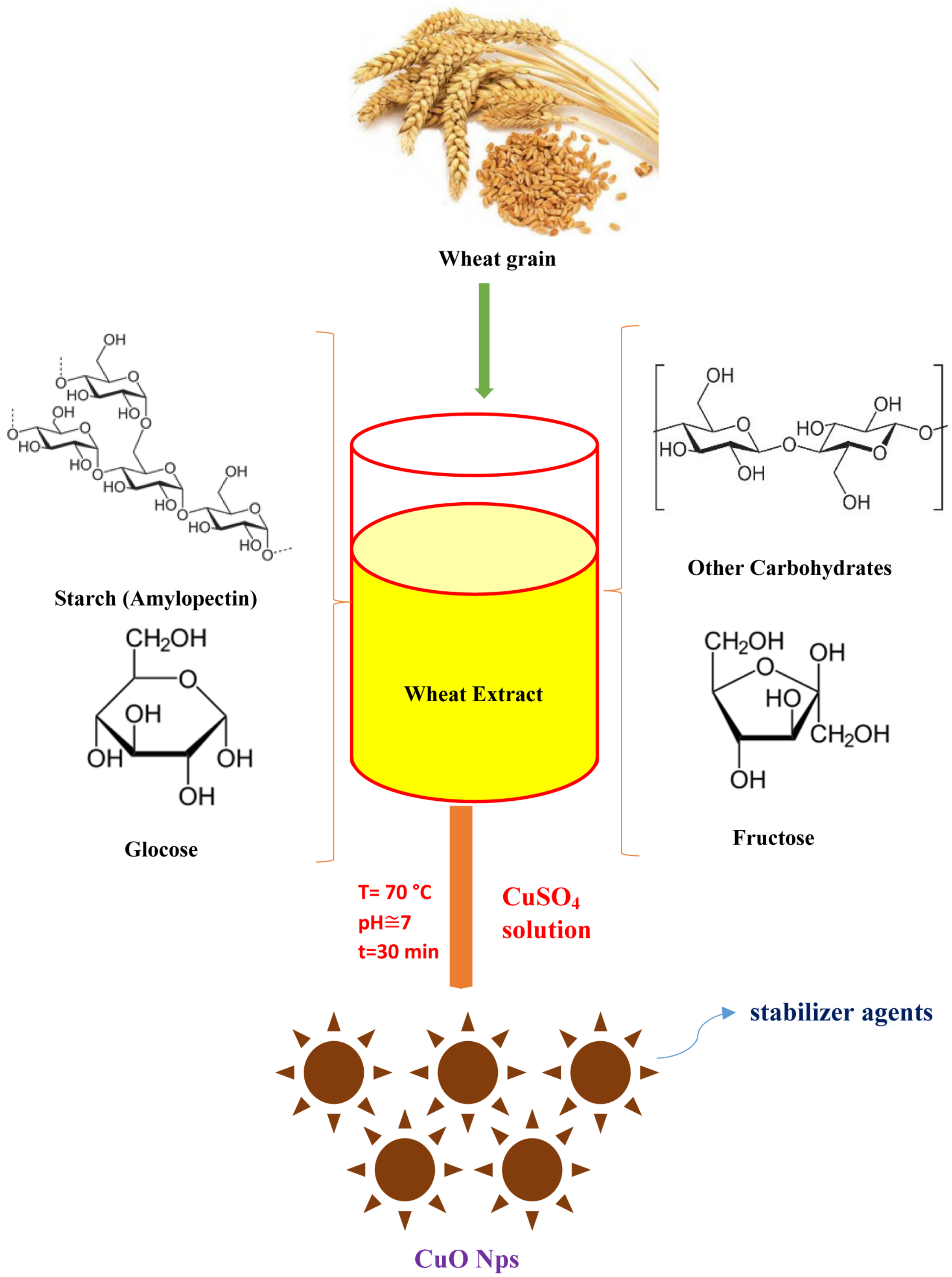
The aqueous extract of wheat seeds was acquired utilizing a facile soaking extraction method [41]. Generally, healthy wheat grains *Triticum aestivum (T. aestivum)* were collected at their harvest time from the local wheat field in Ahwaz (31°19’8.44”N, 48°41’3.12”E), Iran. To obtain the unblemished powder, the surfaces of *T. aestivum* seeds were thoroughly rinsed several times with distilled water to eliminate possible extraneous impurities, for instance, plant detritus, waste or debris of any kind. To reduce seeds moisture content, harvested wheat grain specimens were dehydrated at 60°C for 2 days and grounded to the fine powder using mini flour mill. Afterward, 5 g of sterilized seed powder was soaked in 300 mL of sterile distilled water to prepare an appropriate liquid extract. At a moderate temperature of 80°C, the solution was gently heated for 10 min. Finally, the product was centrifuged at 5000 rpm, filtered, and the obtained supernatant liquid was stored in the fridge at 5°C for more experimental tests.

2.3 Green synthesis of CuO NPs

In the characteristic recipe of wheat seed-mediated biological synthesis of CuO NPs, in an Erlenmeyer flask, 10 mL of liquid *T. aestivum* extract was added into 90 mL of 0.01 M aqueous solution of copper (II) sulfate. The resultant was continually stirred for 1 h at room temperature of 25°C to obtain a homogenous mixture in composition. Then, the solution was sonicated for 10 min and gently heated to 70°C for 20 min. After 10 min of the last heating process, the steady variation in color from dark blue to dark brown into solution was witnessed as an initial visual inspection of bioreduction copper ions to CuO NPs. The resultant was centrifuged at 12000 rpm for 10 min, dried in the furnace at 95°C for 120 min and the precipitate of CuO nanopowder was collected (Scheme 1). In so doing, the reaction was optimized by changing wheat seed extract concentrations, pH, salt precursor concentration, and contact time (see Supplementary material).

2.4 The characterization of CuO NPs

Crystal structure of the bioprepared CuO NPs X-ray was probed using XRD pattern (MPD from analytical). TEM (Zeiss-EM10C-100KV-Germany) and SEM (Zeiss-Sigma-Germany)



Scheme 1: One-pot green synthesis of CuO nanoparticles using aqueous wheat extract.

techniques were used to examine the morphology and particle size of the sample. The surface chemistry of the CuO NPs was investigated using FTIR (VEATOR22-Burker Germany) by a KBr pellet. The formation of CuO NPs was recorded as a function of reaction process time via UV-Vis (Analytic Jena-Germany) in the range of 200-700 nm.

2.5 Catalytic elimination of 4-nitrophenol

To examine the catalytic activity of the biofabricated CuO NPs, in a 100 mL beaker, a 25 mL of 2 mM 4-nitrophenol (4-NP) as a modal pollutant was mixed with 0.2 g $NaBH_4$ under gently stirring for 5 min. Then, 10 mg of CuO NPs were added as catalysts to the reaction mixture under constant stirring at room temperature of 25°C until the yellow color of solution turns to colorless. Next, 2.0 mL sample of the solution was taken out and diluted to 20 mL for further UV-Vis absorption analysis at certain intervals in the recorded scanning range of 200-700 nm. The elimination process of 4-NP was probed via monitoring the alterations in intensity of the major peak at 315 nm as a function of time.

3 Result and discussion

3.1 UV-visible spectrum of CuO NPs

UV-visible spectra of CuO NPs formation *via* the supernatant of the *T. aestivum* extract and crude *T. aestivum* extract were shown in Figure 1. CuO NPs has illustrated a relatively broad absorption peak at 305 nm most likely attributed to surface plasmon resonance (SPR) of CuO semiconductor excitation [42]. Using Tauc relation [43], the optical band gap energy (E_g, eV) of green CuO NPs achieved 4.13 eV (Figure 1c), which was higher value than the corresponding bulk CuO (~2.1 eV) [44]. The increasing *Eg* is attributed to decreasing particle size, thereby, CuO NPs might be

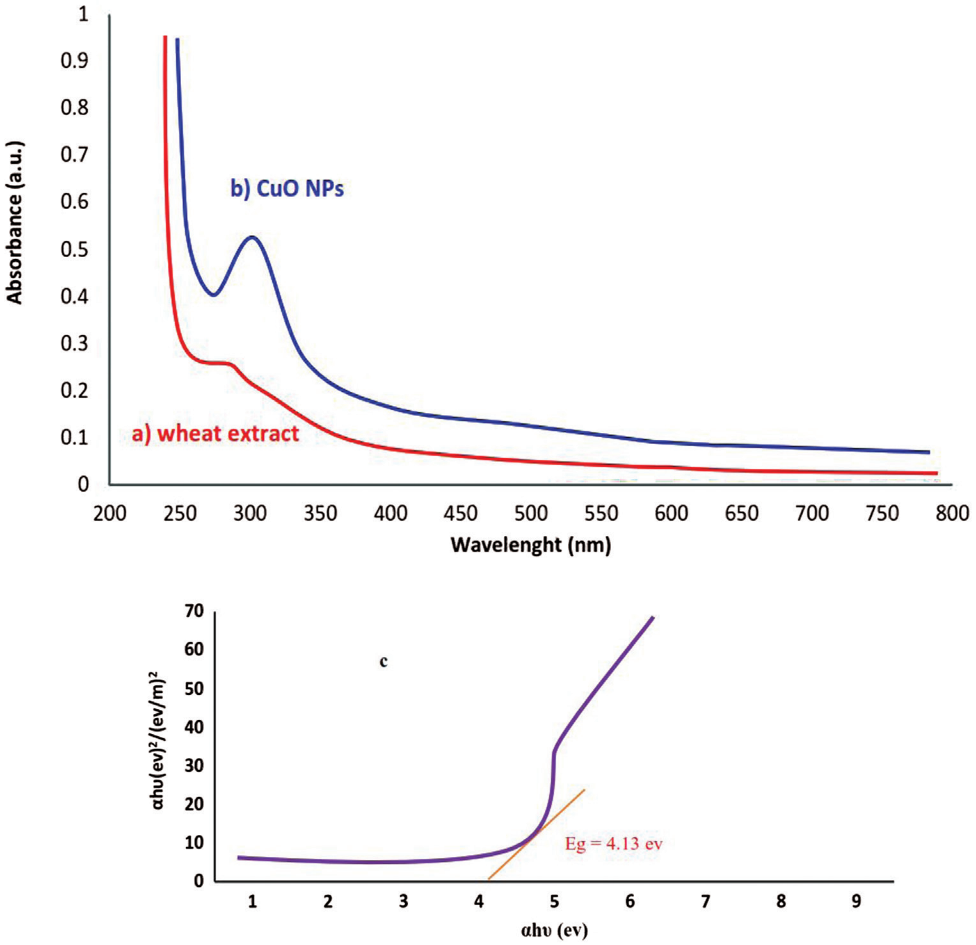


Figure 1: UV–vis spectra of (a) aqueous wheat extract, (b) biofabricated CuO NPs, and (c) Tauc plot of CuO NPs.

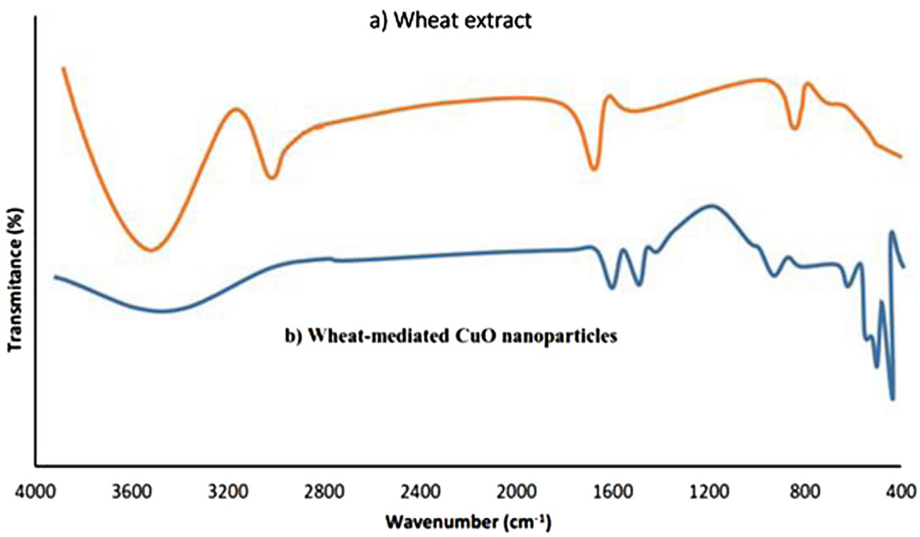


Figure 2: (a) FTIR spectra of wheat extract and (b) wheat-mediated CuO NPs.

used as an ideal harvester for solar irradiations and an effective photocatalyst for environmental remediation [45]. Moreover, UV-vis instrument displays no absorbance peak for pristine wheat seed extract as a blank sample (Figure 1). These observations obviously induce that active organic biomolecules in aqueous extract of wheat seeds were significantly engaged in the reduction of copper cations, Cu^{2+}, to CuO NPs.

3.2 FTIR results

FTIR is a valuable technique to determine active biofunctional groups of wheat seed extract engaged in the copper ions bioreduction and their possible changes after CuO NPs synthesis. CuO NPs and aqueous wheat seed extract reveal a number of bands in different areas of FTIR spectrum, hence demonstrating the tangible dual role of abundant hydroxyls functional groups for synchronous bioreduction of Cu cations and stabilization of as-formed CuO NPs (Figure 2) [46]. In aqueous wheat seed extract (Figure 2a), The 3420, 1640, and 811 cm^{-1} bands were ascribed to O–H (hydroxyl), C=O (carbonyl), and out of plane C–H stretching, respectively. While FTIR spectrum of CuO NPs shows reasonable changes in intensity and position of above peaks along with the presence of new bands in the sample. Bands of 3328, 1552, 1433 and 1032 cm^{-1}, were attributed to O–H (polyol), N–H (amino acid), C–O–(glycosidic linkage), and aromatic or aliphatic C–O stretching, respectively (Figure 4b). In the FTIR spectrum, the characteristic frequencies of CuO bonds of CuO NPs were appeared in 483 (Cu–O symmetric stretching), 541 (asymmetric stretching), and 672 cm^{-1} (wagging) bands, respectively (Figure 2b) [47]. These results evidently indicate an electrostatic interaction between electron-rich amino, ketonic C=O and alcoholic OH groups present in wheat seed extract and Cu ions which in turn leads to biosynthesize of CuO NPs [2].

3.3 XRD examination of CuO NPs

The XRD pattern of biogenic CuO NPs is depicted in Figure 3. The presence of the quite clear and fairly sharp peaks with different 2θ values clearly demonstrated the highly crystalline structure of bio-assisted CuO nanopowder [34]. The analysis of assigned crystal planes (Bragg reflection) of rather strong peaks can be indexed to the monoclinic phase of CuO (JCPDS01-080-1268) [48]. Similarly, X-ray diffraction of biosynthesized CuO NPs *via* an aqueous black bean [23], and *Aglaia elaeagnoidea* flowers extracts revealed that the particles are monoclinic in nature [36]. XRD pattern exhibited no extra peaks, indicating the green CuO NPs were highly purified. Using the Debye-Scherrer formula, the crystal size of CuO NPs of the highest peak at 2 theta = 38.66° (111) was found to be 20.76 nm which fairly smaller than CuO NPs (90.0, 52.0, and 59.8 nm) synthesized by wet chemical precipitation [49], starch extract [50], and flower extract methods, respectively [36].

3.4 XPS analysis of CuO NPs

The purity of the bio-processed CuO nanoproduct was further scrutinized by means of XPS technique as shown in Figure 4. The XPS binding energy at 933.7 and 950.2 eV would assign respectively to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ (Figure 4a). The sharp peak at 530.6 eV is anticipated to O atom bond to copper (II), producing CuO NPs (Figure 4b). These findings are consistent with literature reports [51], confirming the purity of bioproduced CuO NPs. Likewise, Rovani et al. have reported the green synthesis of highly pure silica nanoparticles with high adsorption capacity using sugarcane waste ash

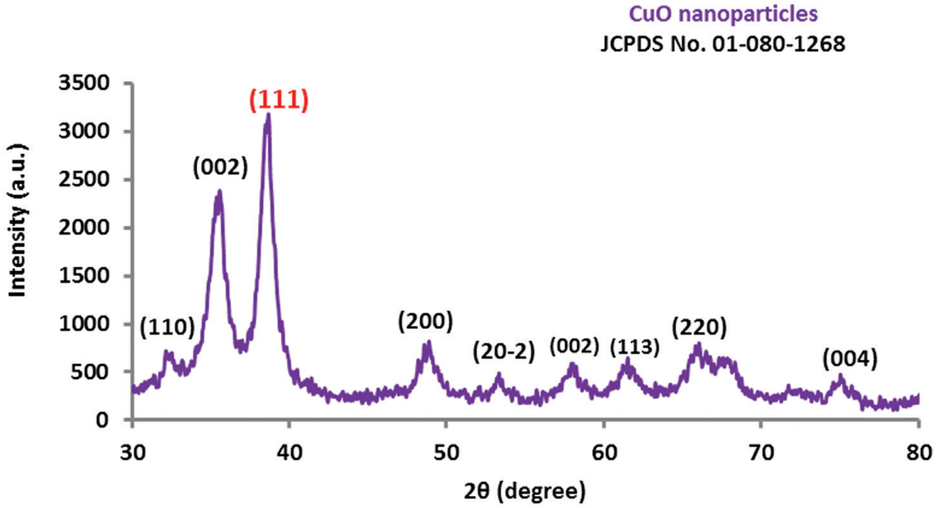


Figure 3: XRD patterns of CuO NPs synthesized by wheat extract.

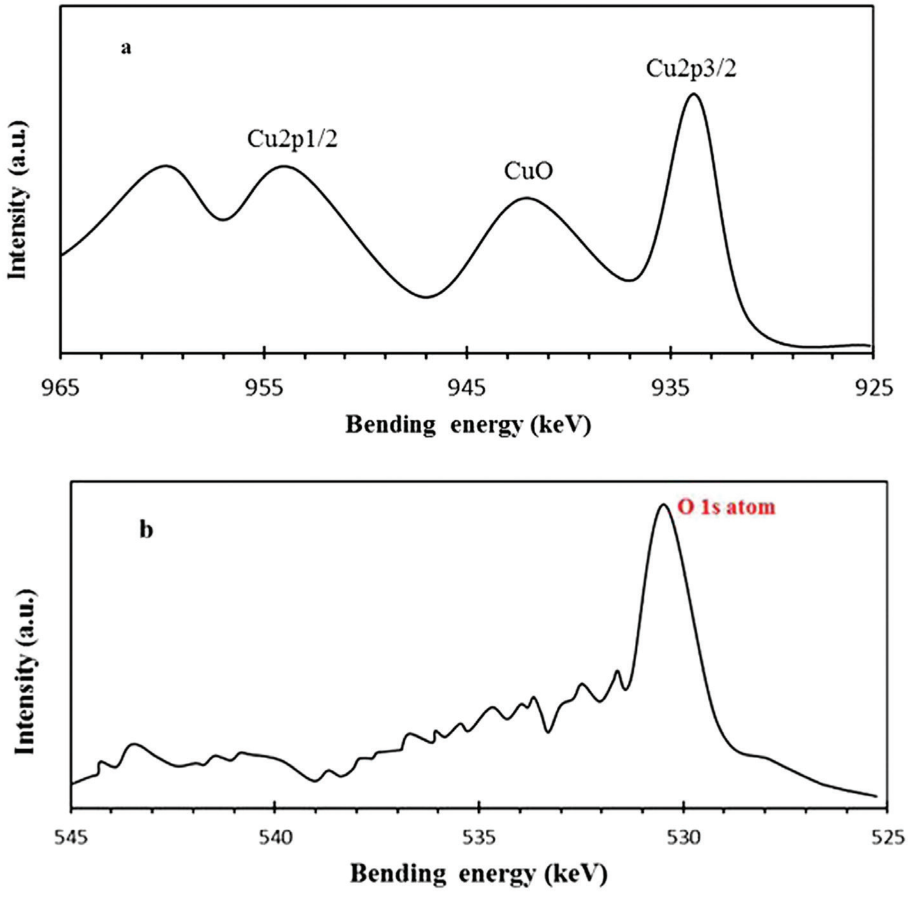


Figure 4: XPS spectra of wheat-mediated CuO NPs, (a) Cu 2P and (b) O 1s.

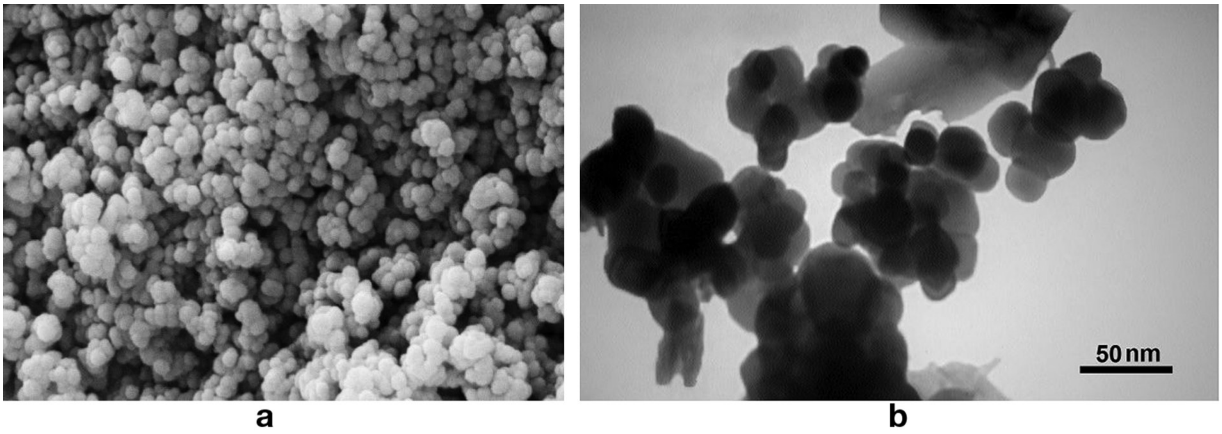


Figure 5: (a) SEM image at high magnification (150x) and (b) TEM micrograph of bio-assisted CuO NPs.

[52]. Moreover, according to the XPS results, no Cu_2O by product was detected in nanoscale CuO specimen (Figure 4).

3.5 SEM and TEM characterizations of CuO NPs

The typical SEM and TEM images of phytosynthesized CuO NPs was depicted in Figure 5. The SEM results revealed the regular spherical shape with the range size approximately from 21 to 42 nm, confirming the formation of CuO NPs by aqueous wheat seed extract (Figure 5a). TEM micrograph clearly indicates the biofabrication of CuO NPs with relatively monodispersed spherical shaped particles and diameter of 5-40 nm measured by 300 particles (Figure 5b). The calculated average particle diameter of CuO NPs was 22 ± 1.5 nm, supporting XRD results (Figure 3). However, due to sample preparation, slight aggregation of particles has arbitrarily arisen in discrete spots.

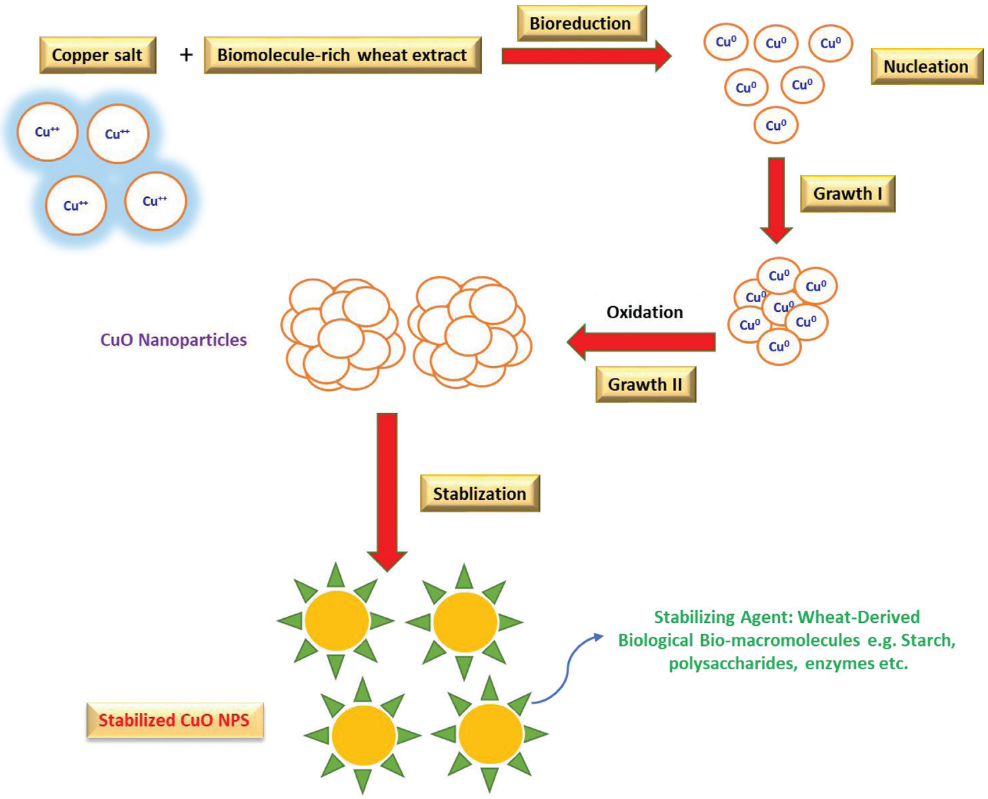
3.6 The mechanism for the formation of CuO nanoparticle

Scheme 1 is depicted as the tentative mechanism for the preparation of CuO NPs. Generally, three stages including activation, growth and termination phase could involve in wheat seed-assisted CuO NPs biosynthesis process (Scheme 2) [53]. In the bioreduction of copper procurer phytochemical compounds presence in wheat seed extract probably function dual role as reducing and capping agents.

In an initial activation step, Cu (II) cations would extract from $CuSO_4$ salt precursor dissolved in DI water. During mixing progression process, the copper ions react with wheat seed-derived bioorganic compounds such as soluble saccharides via an oxidation-reduction mechanism (Scheme 3). For instance, the abundant electron-rich natural biomolecules containing hydroxyl groups with considerable reduction capabilities would reduce copper cations from divalent oxidation state to metallic form which immediately convert to CuO NPs as result of the superior chemical reactivity of bare nanoscale copper metal surface. Evidently, the broad peak of OH of wheat seed extract significantly becomes narrow in FTIR spectrum of CuO NPs indicating an efficient involvement of the alcoholic group in the bioreduction process (Figure 2). In the growth phase, the segregated copper atoms gradually combined to produce CuO NPs. Finally, in the termination step, stabilization of CuO NPs is developed. Wheat seed-derived natural biomacromolecules such as starch with linear and branched structures would surround the nucleated nanoparticles, creating a protective shield and restricting CuO NPs from growth [54]. In addition, the steric forces as a result of those biological macromolecules maintain the capped nanoparticles separated from each other, thus prevents them from agglomeration. This finding is in accordance with preceding reports relating to ZnO and alumina NPs biosynthesis using potato and algal extracts [55,56]. Likewise, Poinern et al. indicated that various bioactive compounds present in food waste are key responsible materials for bioreduction metal ions and stabilization of metallic NPs [57].

3.7 Catalytic activity and reusability of CuO NPs

The catalytic performance of the biofabricated CuO NPs was examined through measuring the degradation of the organic para-nitrophenol pollutant which is documented

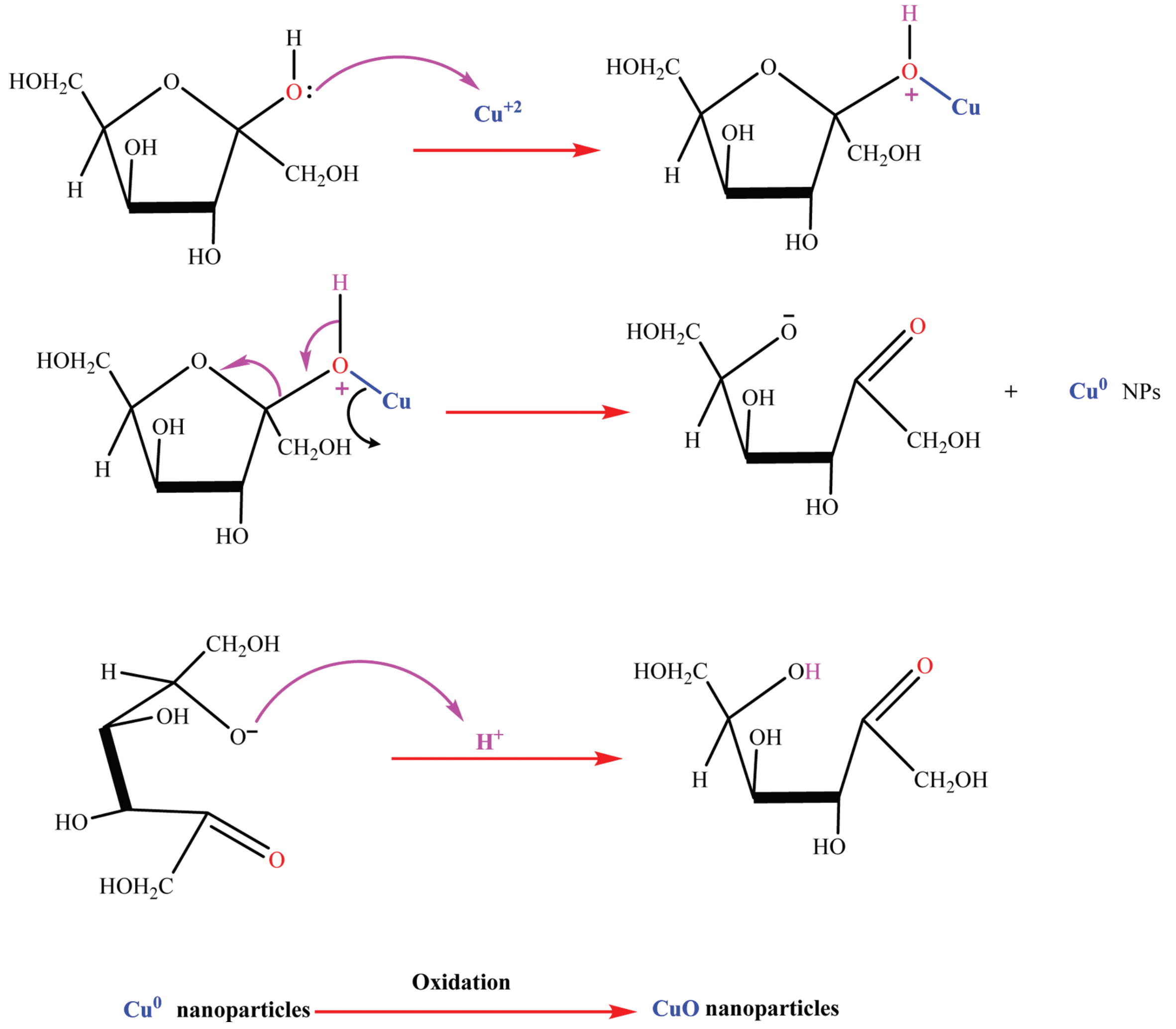


Scheme 2: Illustration of the possible formation mechanism strategy toward biological synthesis of CuO NPs using aqueous extract of wheat seeds.

as a carcinogenic agent to the human being. It is utilized as a precursor for the manufacture of medical products, indicators, and a wide variety of phenetidine and acetophenetidine [58]. Upon the addition of CuO NPs, the intensity of UV-vis absorption peak of 4-nitrophenol at 315 nm was completely disappeared within 20 min, thus indicating the rapid adsorptive removal of an organic 4-nitrophenol pollutant from its aqueous solution (Figure 6). Meanwhile, recyclability of CuO NPs performance toward 4-NP degradation was examined in a UV chamber for five days in a raw. It is found that catalytic activity of the CuO NPs was remarkable (slight changes in removal%), indicating robustness and reusability of biogenic CuO NPs for 4-NP elimination (Figure 7).

3.8 Optimization of CuO NPs synthesis

Evidently, synthesis optimization of reaction is of paramount importance in obtaining desirable shape and size of bioproduced nanoparticles. Accordingly, the optimization process of crucial criteria including pH, salt concentration, contact time and extract concentration was investigated using UV-vis spectrophotometer. In so doing, different pH of 3, 5, 7 and 9 was adjusted by 0.1 N of HCl and NaOH. The absorbance of the resulting solution exhibit that the rate of CuO NPs formation accelerates with increasing pH up to neutral pH = 7 and then gradually reduce (Figure S1). The ionization of functional groups highly likely beyond the reduction of nanoparticle production. The concentration of precursor copper salt was optimized by varying copper sulfate solution (10, 30, 50 and 80 mM) in a constant volume of wheat seed extract (10 mL). Figure S2 has clearly demonstrated that at 50 mM induces the highest amount of CuO NPs on account of readily availability of Cu^{+2} cations. In addition, the concentration of the wheat extract was optimized with the increase in the concentration of the wheat extract solution (10, 15, 20, 25 and 30 mL). The highest absorption is observed at the slightest amount of aqueous extract of wheat seed (10 mL), indicating an efficient activity of bioactive molecules present in extract solution (Figure S3). Time variation of green chemical reaction led to the best quality of shape and size of biofabricated CuO NPs which optimized at a contact time of 25 min (Figure S4).



Scheme 3: Schematic illustration of synthetic steps for bioreduction of copper cations using aqueous wheat extract (wheat-derived fructose as bioreducing agent model).

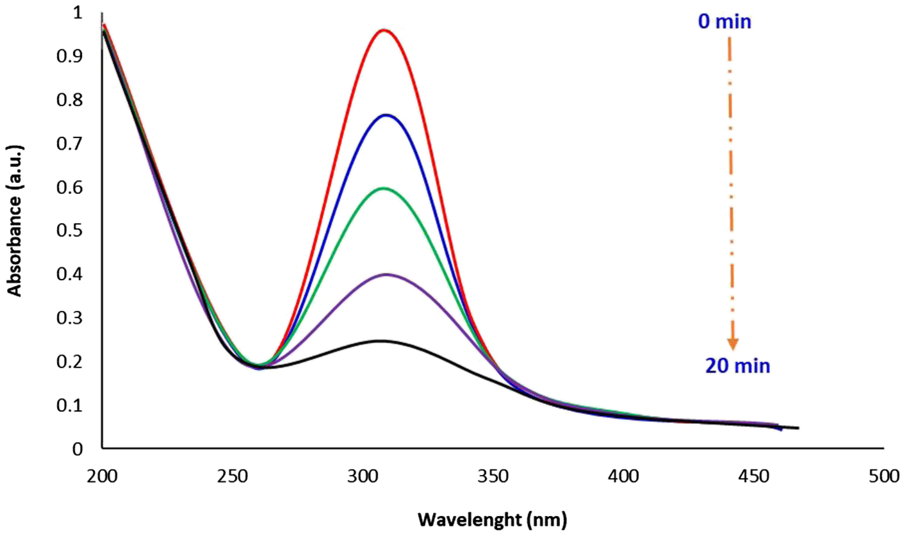


Figure 6: UV-Vis absorption spectral changes during absorption of 4-nitrophenol solution at different times using green CuO NPs.

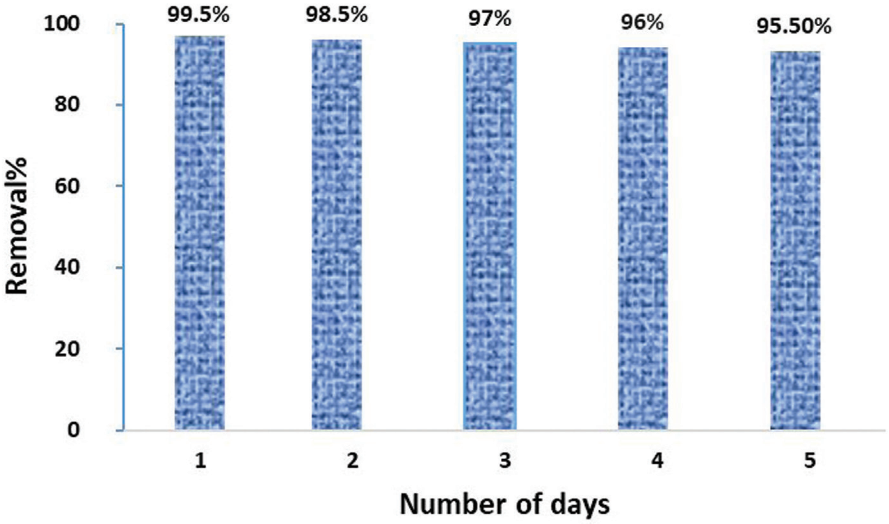


Figure 7: Reusability test of wheat-mediated CuO NPs catalytic efficiency toward 4-nitrophenol pollutant elimination.

4 Conclusion

A simple atom-economy green route for biosynthesize highly stable copper nanoparticles through aqueous wheat seed extract was successfully developed. In this assay, the aqueous wheat seed extract of *Triticum aestivum* showed dual function as reducing and capping/stabilizing agent for the biofabrication of fresh CuO nanoparticles. Copper oxide nanoparticles were obtained under optimal reaction conditions of neutral pH and short time of 25 min at a temperature of 70°C. All standard techniques including UV-vis, FTIR, XRD, SEM, and TEM confirmed the formation of well dispersed CuO nanoparticle. The XRD pattern showed CuO NPs has a monoclinic phase with a crystal size of 20.76 nm. The TEM results indicated the formation of rather spherical NPs with an average diameter of 22 ± 1.5 nm. Visual observations of CuO nanoproduct after three months' storage at room temperature show no dispersion, color change or sedimentation, indicating high steric/electrostatic stabilization of wheat seed extract biomolecules. Optimum conditions for the biosynthesis of CuO NPs are pH = 7, the concentration of $CuSO_4$, 50 mM; wheat extract concentration, 10 mL; and contact time of 25 min. It is found that biogenic CuO NPs exhibited great catalytic efficiency in removal of a toxic 4-nitrophenol pollutant from the contaminated water. Biocompatibility, facile preparation, mild reaction condition, and cost-effectiveness of this approach would open a new window to the biogenic synthesis of a wide range of other inorganic nanoparticles. However, large-scale production of nanoparticles would require more research improving the industrial know-how of plant-based synthesis method.

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Conflict of interest statement: The author declares no conflicts of interest regarding this article.

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