Article

Antioxidant and Organic Dye Removal Potential of Cu-Ni Bimetallic Nanoparticles Synthesized Using *Gazania rigens* Extract

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Abstract: Copper-nickel bimetallic nanoparticles (Cu-Ni BNPs) were fabricated using an eco-friendly green method of synthesis. An extract of synthesized *Gazania rigens* was used for the synthesis of BNPs followed by characterization employing different techniques including UV/Vis spectrophotometer, FTIR, XRD, and SEM. Spectrophotometric studies (UV-Vis and FTIR) confirmed the formation of bimetallic nanoparticles. The SEM studies indicated that the particle size ranged from 50 to 100 nm. Analysis of the BNPs by the XRD technique confirmed the presence of both Cu and Ni crystal structure. The synthesized nanoparticles were then tested for their catalytic potential for photoreduction of methylene blue dye in an aqueous medium and DPPH radical scavenging in a methanol medium. The BNPs were found to be efficient in the reduction of methylene blue dye as well as the scavenging of DPPH free radicals such that the MB dye was completely degraded in just 17 min at the maximum absorption of 660 nm. Therefore, it is concluded that Cu-Ni BNPs can be successfully synthesized using *Gazania rigens* extract with suitable size and potent catalytic and radical scavenging activities.

Keywords: copper-nickel bimetallic nanoparticles; green synthesis; methylene blue; photocatalytic reduction; photocatalysis

1. Introduction

Nanotechnology has introduced many advantages to the fields of physics [1], chemistry [2–4], and the medical sciences [5]. In the late 20th century, the synthesis, application, and commercialization of nanomaterials in different fields have been investigated by many researchers and scientists [6]. Metals have been extensively used over the decades in various fields of chemical science [7,8], biomedical science [9], engineering [10], photonics [11], and electronics [12]. The extensive use of metal-based products in routine life has compelled scientists to find new ways of synthesizing different products. Rather than producing products incorporating metals as macroparticles, nowadays, micro- and nanoparticle-based metal oxides such as CuO and CdO are being produced worldwide [13–16]. Bimetallic nanoparticles have attracted much attention due to their fascinating properties, as the combination of two metals not only creates synergistic effects but also increases

their spectrum of application, such as with respect to their catalytic and antioxidant potential [17–19]. Bimetallic nanoparticle synthesis has played a vibrant role in the development of new materials, especially the composites of different metals. A variety of different bimetallic materials have been reported in which composites of gold, palladium, platinum, and silver [20] have been synthesized, mostly due to their noble surface plasmon resonance properties. Other metals used in bimetallic composites include the metals Fe, Cu, Co, Mo, Sn, Ni, and Zn [21–23].

During recent decades, water contamination has been a major problem in many developing countries around the world [24,25]. We can protect water by its treatment with many different techniques—and nanotechnology is one of them. Recently, different scientists have been searching for solutions to this world-wide problem and have highlighted the importance of nanocatalysts in the field of water treatment, especially for the removal of organic pollutants from water [26]. To address this, a number of different types of novel photocatalytic materials have been proposed for the photocatalytic reduction of organic pollutants and dyes. Cu-Ni BNPs and several novel BNPs produced by the hydrothermal method have been reported for methylene blue reduction by the photocatalytic process [27]. Copper composites with Ni, Fe, Mn, and Co have been developed for the reduction of organic pollutants and dyes [28,29].

Reactive oxygen species (ROS) and free radicals are produced in the human body as a result of many metabolic processes [7]. Free radicals and ROS are now well known to instigate various chronic and degenerative diseases [9] by causing oxidative damage to cellular molecules [10]. The excessive generation of ROS in the human body may result in oxidative stress. To overcome this state of stress and to counter the effects of damaging radicals and reactive oxygen species, antioxidant supplements from external sources are required [11,30–32]. Scientists and researchers are now searching for novel molecules that have antioxidant properties, employing DPPH for scavenging studies [33]. Hence, the current study focuses on the green synthesis of antioxidant-functionalized metal nanoparticles.

Metal nanoparticles belonging to d-block elements in the periodic table include Ag, Au, Pt, and Pd; these are considered noble nanoparticles due to their fascinating properties, but have low cost-effectiveness. In contrast, Cu, Co, Ni, Fe, and Mo metal nanoparticles are cheap, while exhibiting comparable properties to those of noble nanoparticles. Therefore, the current study was designed to synthesize Cu-Ni BNPs using an ecofriendly method of synthesis. In addition, the reduction of methylene blue and scavenging of DPPH radicals using Cu-Ni BNPs have been achieved successfully. Informed by our review of the literature, the research project investigated the application of novel bimetallic nanoparticles for the photocatalysis of organic dye (i.e., methylene blue) reduction.

2. Materials and Methods

2.1. Chemicals and Reagents

Methylene blue (99.99%) was purchased from Fisher Scientific UK. Sodium borohydride (99.9%), DPPH (99.95%), NiSO₄ (99.98%), and CuSO₄ (99.99%) were acquired from Sigma Aldrich Germany. Methanol, used as a solvent, was purchased from Sigma Aldrich Germany.

2.2. Preparation of Plant Extract

Gazania rigens plants were collected from different locations in Lahore, Punjab, Pakistan. After washing, plants were dried under shade and then their constant weight was attained by placing the plants in a hot air oven for 3 h at 60 °C. The plants were then cut and ground to powder. *G. rigens* extract was prepared in methanol using an orbital shaker for 3 h at 150 rpm. The filtrate obtained was dried using a rotary evaporator and stored at −4 °C prior to further use [6].

2.3. Synthesis of Cu-Ni Nanoparticles

A salt solution was prepared by combining NiSO₄ and CuSO₄ in 25 mL of solvent. The extract was dissolved in methanol to prepare a 1000 ppm solution. Both solutions were then

mixed at varying concentrations to determine the optimal salt solution concentration to synthesize bimetallic nanoparticles; the optimal concentration was found to be 200 ppm on the basis of spectrophotometric analysis. The nanoparticles were synthesized by mixing the selected concentrations of the salt and extract solutions. This mixture was then centrifuged and dried [34].

2.4. Instrumentation

The photocatalytic potential of the synthesized nanoparticles was measured by recording the lambda max using a CECIL-7400ce UV-VIS-spectrophotometer under sunlight and by inspecting the FTIR spectra produced by an FTIR spectrophotometer. The X-ray diffraction (XRD) studies were carried out at a scanning rate of 0.05 min^{-1} using a Bruker D8 Advanced diffractometer, equipped with a scintillation counter using Cu K α radiation ($k = 1.5405 \text{ \AA}$, nickel filter) at an acceleration voltage of 30 KV. A NOVA SEM 450 was utilized to obtain SEM images of synthesized BNPs with nanographs obtained for 3 different ranges [35].

2.5. Photocatalytic Reduction of Methylene Blue

The catalytic activity for Cu-Ni BNPs was evaluated following an already published method [36,37]. Solutions of methylene blue (0.086 mM), NaBH₄ (26 mM), and Cu-Ni BNPs at a concentration of 100 ppm were prepared. Using a UV-VIS-spectrophotometer cuvette, 3 mL of methylene blue (acting as a substrate), and 0.4 mL of 26 mM sodium borohydride (acting as a reducing agent), were added. To this solution, containing the substrate and the reducing agent, 0.5 mL Cu-Ni BNP's solution was added, which acted as a catalyst. All the observations were recorded at 665 nm, the maximum absorbance (λ_{max}) for methylene blue [20].

2.6. Radical Scavenging Potential

The antioxidant capacity of the BNPs was studied in terms of their free radical scavenging potential using a 1,1-diphenyl-2-picrylhydrazyl (DPPH) assay [38,39]. Ten milliliters of DPPH (200, 400, and 600 ppm) were taken in three separate flasks and 90 mL of distilled water was added. The mixture was thoroughly mixed and kept in the dark for 30 min. The absorbance was measured later, at 515 nm, against a blank of methanol without DPPH. The results were calculated as the percentage inhibition of the DPPH according to the following equation: % inhibition of DPPH = $[(\text{Abs control} - \text{Abs sample}) / \text{Abs control}] \times 100$, where Abs control is the absorbance of DPPH solution without extracts [40].

3. Results and Discussion

3.1. UV-Visible Analysis of BNPs

Preliminary analysis of the Cu-Ni BNPs was carried out using a UV-visible spectrophotometer to confirm the formation of nanoparticles by the *G. rigens* extract (Figure 1). According to the literature, the absorbance range for Ni nanoparticles is 280–320 nm [41,42]. Therefore, spectra having maximum absorption peaks at 293.5 nm indicated the formation of Cu-Ni BNPs using the *G. rigens* extract.

3.2. FTIR Analysis of Cu-Ni BNPs

The FTIR analysis (Figure 2) of Cu-Ni BNPs was carried out to evaluate the structural bond formations in the BNPs. The spectra were recorded using a Nicolet 5PC, Nicolet Analytical Instrument (Protea, Cambridgeshire, UK) that works in the frequency range of $4000\text{--}400 \text{ cm}^{-1}$. The transmittance at 3095.27 cm^{-1} appeared to be due to the presence of the hydroxyl group and C-H group stretching present in beta-amyrin and cholesterol in the gazania extract [43]; the value at 1662.63 cm^{-1} is due to N-H bending by alkaloids containing amino groups also present in the gazania extract. Additionally, carboxylic acid (-COOH), existing on the boundaries of Cu-Ni BNPs, displays a peak at 859.15 cm^{-1} ; the

peak at 1054.51 cm^{-1} indicates the C–O–C attached to BNPs [39], while the peak appearing at 602.95 cm^{-1} is possibly associated with metal–carbon linkage [44].

Figure 1. The UV-Visible spectrum of Cu-Ni BNPs in the absence of dye.

Figure 2. The FTIR spectrum of copper-nickel bimetallic nanoparticles.

3.3. X-ray Diffraction Analysis

The X-ray diffraction patterns of Cu-Ni, as synthesized nanoparticles, were recorded in 2θ values ranging between 20° and 80° at a scan rate of 0.4° per minute via continuous

scan type. According to Figure 3, the sharpness of peaks corresponds to the phase purity and crystal structure for the particular catalytic sample. The peaks appearing at 29° (110), 43° (200), 46° (100), 52° (210), 69° (111), and 74.4° (211) correspond to copper [4,45]. The peaks observed at 52° (200), 46° (100), 52° (100), 57° (210), and 61° (210) correspond to face-centered cubic Ni nanoparticles [41,46,47]. Mixing of Cu and Ni nanoparticles in a single compound displayed a single-phase system but both Cu and Ni maintained their crystallinity. However, appearance of new major peaks at 33° and 62° at 200 and 210 planes illustrates the influence of both Cu and Ni elemental composition in the crystal lattice.

Figure 3. The XRD diffraction pattern of Cu-Ni BNPs.

Additionally, the crystallite size “D” of the as-synthesized nanoparticles was estimated from XRD analysis by examining major peaks using the Debye–Scherrer equation given in Equation (1).

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where k represents the constant shape factor equal to 0.9, λ is the X-ray wavelength, β indicates the full width half maximum (FWHM), and θ represents the Bragg’s angle. The crystallite size was found to be 47 nm.

3.4. Morphological Analysis

The SEM images for Cu-Ni BNPs presented in Figure 4a–c were obtained in three different magnifications (30 nm, 50 nm, and 100 nm). These images provide data regarding the morphology of the nanoparticles. The images appear as a heterogeneous mixture. The particle sizes vary due to the clumping of nanoparticles. The surface of the particles has not remained smooth, which may be due to their interaction with the extract [48]. However, according to the SEM results, the size of nanoparticles predicted ranged from 50 nm to 100 nm.

Figure 4. SEM nanographs of Cu-Ni BNPs with scale bars of (a) 30 nm, (b) 50 nm, and (c) 100 nm.

3.5. Photocatalytic Reduction of Methylene Blue in Aqueous Medium

Contamination of water by organic pollutants results in adverse effects not only for aquatic life but also for humans. Organic pollutants include pharmaceuticals, detergents, pesticides, industrial waste, and dyes [26]. Dyes may cause carcinogenic effects having benzene rings in their structure. Therefore, their removal from the aqueous medium is essential, and photocatalytic reduction is widely performed to achieve this. In the reduction of methylene blue (MB) dye, the reducing agent NaBH_4 has a primary role, but it requires the support of a catalyst to complete the reduction [49,50].

In the current study, MB reduction was observed in the presence of NaBH_4 without a catalyst and showed no reduction (Figure 5). This may be due to no transference occurring of electron pairs from BH_4^- to the azo group of the MB. Correspondingly, as illustrated in Figure 5b, there is also no reduction in the absence of a reducing agent, because no electron pair is present. Both of these reactions were monitored under controlled conditions. These exemplary reactions suggest that the reduction may only be possible in the presence of a catalyst.

Figure 5. (a) 0.086 mM MB, 13 mM NaBH_4 , and no Cu-Ni bimetallic nanocatalyst; (b) 0.086 mM MB, 100 ppm Cu-Ni bimetallic nanocatalyst, and 0 mM NaBH_4 .

Nanoparticles act as catalysts due to their high surface-to-volume ratio and smaller sizes are helpful in the reduction of dyes in water [51]. The reduction of MB was achieved using Cu-Ni BNPs in the presence of NaBH_4 . The reduction reaction was completed in 17 min. No reduction phenomenon was observed in the first 5 min while the catalyst stabilized/adjusted with the dye molecules until the generation of reactive oxidation species (ROS) involved in the photocatalytic reduction (Figure 6), which reflects the excellent capability of the Cu-Ni nanocatalyst [52]. This is referred to as the induction period where the reduction phenomenon is slow, accelerating afterwards [53–55]. Here, the catalyst acts as a carrier which transfers an electron pair from borohydride to the substrate and

thus enables the leuco form of methylene blue to be formed. The leucomethylene blue is not harmful.

Figure 6. UV-Vis spectra for the MB photocatalytic reduction using 100 ppm Cu-Ni bimetallic photocatalyst, 13 mM NaBH_4 , and 0.086 mM MB.

A kinetic study was also performed for the model-controlled reaction of MB reduction on the surface of Cu-Ni BNPs. As the reaction proceeds, absorbance at 665 nm decreases due to the charge transfer from the reductant to the reactant (MB). The reaction follows the Langmuir–Hinshelwood mechanism having pseudo first order reaction kinetics because concentration of sodium borohydride was 150 times greater than that of the methylene blue, $[\text{NaBH}_4] \gg [\text{MB}]$. The graph presented in Figure 6 provides information about the reaction from the first stage (adsorption of the reactant to the nanocatalyst), the intermediate stage (interaction between the reactant and the reductant, i.e., the reaction time) to the end stage (reaction completion and desorption of the reactant). The slope gives the value of the experimental rate constant (k_{exp}) 0.2505 min^{-1} with a half-life of 2.7664 min (Figure 7).

3.6. Radical Scavenging Potential

Free radicals are unstable and tend to form stable bonds by accepting or donating available electrons. Nanoparticles, being zero valent and capable of donating electrons to free radicals, inhibit the initiation step of oxidative chain reactions and the formation of stable free radicals. The DPPH is a stable, nitrogen-centered free radical which has a very strong absorption band at 517 nm. The antioxidant activity of any species can be determined using spectrophotometry to assess the change in color of DPPH from violet to yellow. The change in color is attributed to the reduction of DPPH either by hydrogen or electron donation [56,57]. The DPPH radical inhibition potential of varying BNP concentration is presented in Figure 8a–c. The radical scavenging potential of BNPs is reflected in increased reaction time, as evidenced in the figures, with maximum scavenging observed after 30 min of reaction. Radical scavenging can be enhanced by increasing the concentration of BNPs [58].

Moreover, the position for the UV-Vis absorption maximum varies with different factors such as the nature and concentration of the solvent/s, the nature of the radical, the intensity of light, etc. [59,60]. Consequently, the position for the absorption maximum moved from 540 to 550 nm with an increase in the DPPH concentration from 200 to 600 ppm. Incident light was adsorbed for one minute before undergoing the absorption process, which produced the absorption signal at a lower wavelength, which might be attributed to a less stable form of DPPH radical [61,62]. Once the DPPH is stabilized by the antioxidant, it absorbs at a longer wavelength; i.e., a red-shift occurs [63].

Figure 7. A kinetic model of the photocatalytic reduction at fixed concentrations with concentrations of MB = 0.086 mM, NaBH_4 = 13 mM, and 100 ppm of Cu-Ni bimetallic nanocatalyst.

Figure 8. Antioxidant activity of Cu-Ni BNPs at (a) 200, (b) 400, and (c) 600 ppm of DPPH.

The reaction between DPPH and Cu-Ni BNPs (antioxidant) (Figure 9) follows second order kinetics, as the concentrations of both the reactants are in the same proportions. All the reactions were noted at around 550 nm after an interval of 10 minutes. The concentration of DPPH used ranged from 200 to 600 ppm. In Figure 9, $\ln [\text{DPPH}]_t / [\text{DPPH}]_0$ is presented as a function of time that provides a value of the experimental rate constant and the half-life,

as indicated in Table 1. The comparison of different reported photocatalysts using our synthesized nanoparticles for dye reduction has been represented in Table 2.

Figure 9. Correlation between concentration and time at different ppm values.

Table 1. Estimation of kinetic parameters of BNPs radical scavenging potential.

Concentration (ppm)	k_{app} (min^{-1})	Half Life ($t_{1/2}$) (min)
200	0.0082	84.51
400	0.0103	67.28
600	0.0114	60.78

Table 2. Comparison of various photocatalysts for dye reduction.

Composite	Dye Conc.	Conc. of Catalyst	Time (min)	Light	Ref.
Ag NPs	100 mg/L	10 mg/100 mL	120	Sunlight	[64]
ZnO	0.5 μM /50 mL	15 mg/100 mL	70	UV	[65]
CoMn ₂ O ₄ NPs	1.370×10^{-5} M	0.05 g/100 mL	120	Sun-light	[66]
rGO-Fe ₃ O ₄ /TiO ₂	5.5 ppm	15 mg/100 mL	55	500 W mercury bulb	[40]
Cu-Ni BNPs	0.086 mM	100 ppm	17	Sunlight	This work

4. Conclusions

Nickel–copper bimetallic nanoparticles, prepared via a green synthetic route using *Gazania rigens* extract, were found to be effective in biological and photocatalytic activities. Sharp peaks in XRD pattern indicated the crystalline morphology of the Cu-Ni BNPs. The percentage transmittance in the FTIR analysis indicated the presence of carbonyl groups along with metal bond vibrations. SEM micrographs confirmed the formation of a heterogeneous surface that facilitated the catalytic process. In addition, the particle size estimated from the SEM images was found to be in the range of 50 to 100 nm. The photocatalytic potential of Cu-Ni BNPs were investigated by studying the photocatalytic reduction of methylene blue under visible light irradiation. The BNPs were found to be highly efficient photocatalysts degrading the MB in only 19 min with a rate constant of 0.2505 min^{-1} . This implies that they are superior to several chemical nanoparticles, as well as having a greener process of synthesis. In addition, the synthesized nanoparticles were investigated for their scavenging potential for DPPH radicals and were found to be applicable to the radical scavenging purpose. Therefore, the Cu-Ni BNPs synthesized from greener routes have been found to exhibit excellent photocatalytic potential. Such BNPs,

being more cost effective, simple, and ecofriendly, could be employed as photocatalysts for the reduction of several organic dyes in industrial wastewater bodies.

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