Cu-Doped 1D Hydroxyapatite as a Highly Active Catalyst for the Removal of 4-Nitrophenol and Dyes from Water

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ABSTRACT: Metallic copper nanoparticle (Cu NP)-doped 1D hydroxyapatite was synthesized using a simple chemical reduction method. To describe the structure and composition of the Cu/HAP nanocomposites, physicochemical techniques such as X-ray diffraction, Fourier transform infrared spectroscopy, inductively coupled plasma, N₂ adsorption–desorption, X-ray photoelectron spectroscopy, and high-resolution transmission electron microscopy were used. The TEM scan of the Cu/HAP nanocomposite revealed a rod-like shape with 308 nm length and 117 nm width on average. The catalytic activity of Cu/HAP nanocomposites for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in the presence of NaBH₄ has been thoroughly investigated. The 0.7% Cu/HAP nanocomposite was shown to have superior catalytic activity than the other nanocomposites, converting 4-NP to 4-AP in ~1 min with good recyclability. Moreover, this nanocomposite showed excellent catalytic performance in the organic dye reduction such as Congo red and acriflavine hydrochloride dyes. The high dispersion of Cu NPs on HAP support, the high specific surface area, and the small Cu particles contributed to its remarkable catalytic performance.

1. INTRODUCTION

The rapid development of industry and modern technology has recently resulted in major environmental issues such as water and air pollution. Industrial discharges, which have significant levels of toxic heavy metals, nitroaromatic chemicals, and organic dyes, are the primary source of water contamination. 4-Nitrophenol (4-NP) is a prominent class of environmental pollutants that is widely employed as an intermediate for several industries, including dyes, pharmaceuticals, pigments, pesticides, and polymers. Due to the importance of these substances, there are no replacement for these compounds in human life. Removal of such pollutants from aquatic systems is very difficult because of their biological and chemical stability. Furthermore, 4-NP is highly toxic toward humans, animals, and plants because it can cause blood disorders, headache, and severe central nervous system, liver, and kidney damage. Therefore, it is important to remove such pollutant from wastewater or at least convert it to a less-toxic substance or to any value-added chemical products for reuse. In this context, 4-aminophenol (4-AP), a reduced version of 4-NP, can be employed as a starting material for a range of essential compounds, including drugs, dye stuffs, photographic developer, rubber chemicals, corrosion inhibitors, and hair coloring agents.

The most promising, effective, and environmentally benign method for removing hazardous organic compounds from industrial effluents is the reduction of 4-NP to 4-AP. However, it is difficult to perform this reduction reaction at ambient conditions; thus, an efficient catalyst is essential for such reaction. Several studies have investigated the efficacy of noble metal nanomaterials as catalysts for 4-NP reduction, such as Pd, Au, Ag, Pt, and Ru. However, some of these.
catalysts are less abundant, expensive, and less resistant to poison, which leads to decreasing or losing their catalytic activity and stability.\textsuperscript{5} Copper nanoparticles (Cu NPs) are a cheaper, highly abundant, and competitive alternative to various rare and expensive noble metal catalysts in different applications. Unfortunately, pristine Cu NPs are thermodynamically unstable and are prone to agglomeration and coalescence,\textsuperscript{11,12} losing their catalytic activity. To overcome this drawback and getting highly dispersed small Cu particles, a specific supporting material should be used.\textsuperscript{12} In consequence, different supports have been used to disperse Cu nanoparticles, which include graphene,\textsuperscript{13} graphene oxide,\textsuperscript{14} activated carbon,\textsuperscript{15} CNTs,\textsuperscript{16} and so forth.

Hydroxyapatite (HAP) (Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{2}) has emerged as a novel catalytic support owing to its exciting features such as low solubility in water, high thermal stability, high ion-exchange ability,\textsuperscript{16} great adsorption capacity,\textsuperscript{17} tunable specific surface area and porosity, and adjustable acidity and alkalinity.\textsuperscript{18} Some successful studies using HAP as a support for metal nanoparticles for application in the reduction of 4-NP were found in the literature. For instance, Bahadorikhalili et al.\textsuperscript{19} successfully synthesized Ag NP-decorated thiourea-functionalized magnetic HAP that can reduce 4-NP with a rate constant $k = 0.025$ s$^{-1}$. Das et al.\textsuperscript{20} decorated HAP with Ag NPs by a facile green method for the reduction of 4-NP and organic dyes. They found that the prepared catalyst can reduce 4-NP in 5 min with a $k$ value equal to 0.0073 s$^{-1}$. Das et al.\textsuperscript{21} found that the Cu/HAP/ZnFe\textsubscript{2}O\textsubscript{4} nanocomposite showed excellent activity toward 4-NP reduction. They demonstrated that the nanocomposite has the ability to complete the 4-NP reduction in $\sim$5 s. Ag NPs anchored on layered double hydroxides, and HAP was employed for the 4-NP reduction by Hoang et al.\textsuperscript{22} They found that the catalyst contains 4 wt % Ag and exhibits the highest catalytic performance in $\sim$7 min with a rate constant $k = 0.0076$ s$^{-1}$. The HAP nanowire/Au NP-layered paper was investigated by Xiong et al.\textsuperscript{23} in the catalytic reduction of 4-NP as a high-efficiency catalyst using a continuous flow method. Furthermore, the Cu-based materials showed a high catalytic performance for the reduction of 4-NP. Some of the recent papers include Cu-COF\textsubscript{24}, Cu\textsubscript{6}S\textsubscript{8}\textsuperscript{25} CNF/PEI\textsubscript{26}-Cu,\textsuperscript{26} Cu-Cu\textsubscript{2}O,\textsuperscript{27} Cu-doped glass,\textsuperscript{28} Cu NPs/SG,\textsuperscript{29} Cu-ICAI,\textsuperscript{30} Cu NPs/boron nitride,\textsuperscript{31} PZS@Ag-Cu NP composites,\textsuperscript{32} and Cu/ZnO.\textsuperscript{33} However, the application of Cu/HAP as a catalytic system for the reduction of 4-NP has not yet been reported, to our knowledge. Therefore, the main aim of the current work is to prepare the Cu/HAP nanocomposites which may have remarkable potential to reduce organic pollutants in water at an ambient temperature. The nanocomposites were used as effective recyclable catalysts to reduce harmful compounds such as 4-NP and organic dyes. The effect of various parameters on 4-NP reduction was studied, including the amount of Cu NP content and the weight of the nanocomposite.

2. EXPERIMENTAL SECTION

2.1. Materials. Calcium nitrate tetrahydrate (Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O, Lachema Brno), ammonium dihydrogen orthophosphate (NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}, ADWIC), ammonium hydroxide (NH\textsubscript{3}OH, 25% NH\textsubscript{3}, BDH AnalR), and cetyltrimethylammonium bromide (CTAB, Merck) were used without additional purification in the 1D hydroxyapatite (1D HAP) synthesis. Copper nitrate trihydrate (Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O, assay: 98%, Laboratory Chemicals) and ascorbic acid (assay: 98%, Alpha Chemicals) were used for the synthesis of Cu NPs. 4-NP (assay: 98%) and sodium borohydride (NaBH\textsubscript{4}, assay: 98%) were obtained from Research-Lab Fine Chem Industries (India) and SDFCL, respectively. Sigma-Aldrich (Germany) provided the organic dyes (Congo red and acriflavine hydrochloride, ACF).

2.2. Synthesis of 1D HAP. The cationic surfactant approach was used to synthesize the 1D HAP particles with some modifications to the procedure previously reported by Gopi et al.\textsuperscript{34} First, 50 mL of 0.024 M NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4} solution containing 0.024 M of CTAB was prepared using double-distilled water at 50 °C under steady stirring for 1 h. Under vigorous stirring, 50 mL of Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O solution (0.04 M) was gently added dropwise to the aforementioned solution mixture, and then ammonia solution was added dropwise to a pH $\sim$10. The precipitate was then aged for 2 h, before being filtered and rinsed with ethanol and bi-distilled water. The white precipitate was dried for 48 h at 80 °C before being calcined at 900 °C for 2 h.

2.3. Synthesis of Cu NP-Doped 1D HAP. In a typical preparation process, predetermined amounts of Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O with various weights consistent to the theoretical yield of (0.3\%–1\%) Cu NPs/HAP were dissolved in 50 mL of bi-distilled water under stirring at room temperature. A calculated weight of 1D HAP powder was disseminated in the Cu\textsuperscript{2+} solution under strong stirring for 30 min to allow the Cu ions to completely adsorb on the HAP surface. Thereafter, the ascorbic acid solution having a concentration 5 times that of the copper nitrate solution was gradually added into the copper nitrate aqueous dispersion of 1D HAP. The reduction reaction was performed at 90 °C under continuous stirring for 3 h. When the solution had cooled to room temperature, the precipitate was filtered through a filter paper, washed several times with ethanol and double-distilled water, and dried for 2 h at 80 °C.

2.4. Characterization. X-ray diffraction (XRD) of the pure 1D HAP and Cu-doped HAP was performed in the angle range of 2θ 4–80° using an X-ray diffractometer, PW 2103, Philips, The Netherlands, with CuK radiation, $\lambda=1.5406$ Å.

Using a Nicolet spectrophotometer, model 6700, in the range of 4000 to 400 cm$^{-1}$ via the KBr pellet technique, the different functional groups present on the pure 1D HAP and Cu-doped 1D HAP were assessed using Fourier transform infrared (FTIR) spectroscopy.

The actual Cu contents on the Cu/HAP nanocomposites were estimated by inductively coupled plasma (ICP) on Thermo Scientific iCAP 6200.

The specific surface area measurements were made by N\textsubscript{2} adsorption study using BET analysis techniques on a Nova 3200 instrument (Quantachrome Instrument Corporation, USA).

The surface electronic structure and the chemical states of the pure 1D HAP and 0.7% Cu/HAP nanocomposite were recorded via X-ray photoelectron spectroscopy (XPS) using a monochromatic X-ray Al K-alpha source (∼10 to 1350 eV) (K-ALPHA, Thermo Fisher Scientific, USA). The measurements were carried out under vacuum at a base pressure of around 10$^{-6}$ Torr.

Transmission electron microscopy (TEM) images were taken on a JSM-2100 JEOL electron microscope (Japan).

2.5. Catalytic Performance of Cu NP-Doped 1D HAP. The reduction of 4-NP to 4-AP in the presence of NaBH\textsubscript{4} was used to assess the catalytic performance of the Cu NP-doped
1D HAP. During the reaction, 1 mL of $1 \times 10^{-2}$ M of 4-NP solution was added to 100 mL of 0.1 M NaBH$_4$ in a beaker, and this leads to an intense yellow color. The reaction progress is assessed by removing a small portion of the reaction mixture after a set amount of time and measuring the absorbance with UV–vis absorption spectroscopy at a scanning range of 200–600 nm. The reduction efficiency percentage of 4-NP to 4-AP was calculated by eq 1

$$\text{Reduction efficiency}(\%) = \frac{A_0 - A_t}{A_0} \times 100$$ (1)

where $A_0$ denotes the initial absorbance of 4-NPL at max = 400 nm and $A_t$ denotes the absorbance at various time intervals ($t$).

3. RESULTS AND DISCUSSION

3.1. Characterization of the Prepared Catalysts. The XRD patterns of the 1D HAP and Cu/HAP nanocomposites are presented in Figure 1. The XRD pattern of the prepared

![XRD diffraction patterns of pure 1D HAP and Cu/HAP nanocomposites.](image)

1D HAP shows the crystalline phase corresponding to hexagonal Ca$_{10}$$(PO$_4$)$_6$(OH)$_2$ with lattice parameters $a = 9.4600$ Å and $c = 6.8800$ Å and a space group of P6$_3$/m according to the standard JCPDS no 09-0432. The main characteristic peaks of 1D HAP were observed at $2\theta = 25.7$, $31.5$, $32.6$, $33.8$, $46.4$, and $49.3^\circ$, which can be ascribed to the (002), (211), (112), (300), (202), (222), and (213) crystalline planes, respectively. The intensity of the diffracted peaks characterizing the (211) and (002) planes are equal to 100 and 40 units, respectively, and the $I_{(211)}/I_{(002)}$ ratio is 2.5, which is consistent with the standard HAP. The XRD pattern of the Cu/HAP nanocomposites showed only diffraction peaks corresponding to 1D HAP, and the peaks related to Cu species cannot be detected. This phenomenon could be attributable to the high dispersion of Cu NPs on the surface of 1D HAP or the fact that their concentrations are less than the instrument’s detection limit.

It was also noted that the diffraction peaks displayed by the nanocomposites become sharper, especially the peak at a $2\theta$ value of $32.6^\circ$, which reflects that the crystallinity as well as the crystalline size increases by doping 1D HAP by Cu NPs. Furthermore, the average crystallite sizes of 1D HAP, 0.7% Cu/HAP, and 1% Cu/HAP were calculated as 21.9, 23.2, and 26.5 nm, respectively, using the Scherrer equation.

The FTIR spectra of the pure 1D HAP and Cu/HAP nanocomposites are displayed in Figure 2. The spectrum of the pure 1D HAP shows bands located at 475 and 961 cm$^{-1}$, which are ascribed to the $\nu_2$ and $\nu_1$ vibration modes of the PO$_4^{3-}$ group. The bands located at 1041 and 1089 cm$^{-1}$ are due to the phosphate group’s $\nu_3$ mode. At 565, 602, and 632 cm$^{-1}$, the phosphate group’s $\nu_4$ vibration mode was observed. The bands observed at 1635, 3420, and 3570 cm$^{-1}$ are characteristic to the vibrational modes of the O–H bending, adsorbed lattice water, and O–H stretching, respectively. The carbonate group is responsible for the appearance of the band around 1456 cm$^{-1}$. It was proposed that the carbonate group was formed during the synthesis operations by a reaction between ambient CO$_2$ and the solution. In addition, two bands were detected at 2853 and 2923 cm$^{-1}$ and can be designated to the C–H vibration, which indicates the existence of CTAB surfactant in HAP. The FTIR spectra of the Cu/HAP nanocomposites, on the other hand, are similar to the spectrum of 1D HAP, where only HAP’s distinctive bands can be found. This finding is in good agreement with the results of Bee et al., they found that the FTIR spectra of the HAP/Ag NP nanocomposites are comparable to that of HAP but do not involve the development of new bands.

ICP was used to determine the actual Cu contents on the Cu/HAP nanocomposites, and the obtained results are presented in Table 1. The results indicated that the actual Cu contents were slightly lower than the theoretical ones.

The specific surface area ($S_{\text{BET}}$) of 1D HAP and the Cu/HAP nanocomposites are displayed in Table 1. The $S_{\text{BET}}$ value of 1D HAP is 4.2 m$^2$ g$^{-1}$ and increases continuously (from 4.2 to 9.6 m$^2$ g$^{-1}$) with increasing Cu NP loading from 0 to 0.7 wt %. Further increasing the percentages of Cu NPs to 1 wt %, the $S_{\text{BET}}$ value of the nanocomposite slightly decreased to 8.6 m$^2$ g$^{-1}$, suggesting that metal addition resulted in partial pore blockage.

The XPS technique was used to analyze the chemical states and surface composition of the pure 1D HAP and 0.7% Cu/HAP nanocomposites, and the resulting spectra are depicted in Figure 3. The full survey showed the presence of calcium (Ca 2p), phosphorous (P 2p), oxygen (O 1s), and carbon (C 1s) in both the samples (Figure 3a). For the 0.7% Cu/HAP nanocomposite, a new peak related to copper (Cu 2p) was also detected. Moreover, the peak intensity related to Ca, P, O, and C decreased in this sample. The high-resolution XPS scan of the Ca 2p region (Figure 3b) showed two peaks at 348 and 351.8 eV for the pure 1D HAP, which are corresponding to the
Ca $2p_{1/2}$ and Ca $2p_{3/2}$ regions of the calcium phase on HAP, respectively. For the 0.7% Cu/HAP nanocomposite, the binding energies of Ca $2p_{1/2}$ and Ca $2p_{3/2}$ increased from 348 and 351.8 eV to 349.5 eV and 352.9 eV, respectively. The shift toward higher binding energy for the 0.7% Cu/HAP nanocomposite indicates an increase in the crystallinity of this sample. This observation is consistent with that obtained from XRD analysis; doping HAP by Cu NPs increases the crystallinity of the sample (Figure 1). Figure 3c shows that the high-resolution XPS scan of the P 2p region represents peak at 134.2 eV for the pure 1D HAP, which is attributed to the phosphate group in HAP. This peak shifted to 135.4 eV in the spectrum of the 0.7% Cu/HAP nanocomposite. The O 1s XPS spectrum (Figure 3d) has three distinct signals at 531.1, 532.5, and 533.2 eV for the pure 1D HAP, which belonged to the Ca–O bond, P–O bond, and O–H fingerprint of HAP, respectively. However, in the 0.7% Cu/HAP nanocomposite, the binding energies at 532.5 and 533.2 eV increased to 533.2 and 536 eV, respectively. The C 1s XPS spectrum (Figure 3e) shows three signals at 289.6, 286.6, and 285.2 eV for the pure 1D HAP, respectively, which belonged to the C–O binding of CO$_3^{2-}$ adsorbed in HAP, the C–OH and C–O–C bindings, and the surface contamination of the type C–C and C–H bindings. The peaks at 289.6 and 286.6 eV

| catalyst          | $S_{BET}$ (m$^2$/g) | crystallite Size (nm) | theoretical Cu (%) | actual Cu (%) | $t_{completion}$ (min) | efficiency (%) | $k_{app}$ (min$^{-1}$) | $R^2$ |
|-------------------|----------------------|-----------------------|---------------------|---------------|------------------------|----------------|--------------------------|------|
| 1D HAP            | 4.2                  | 21.9                  | 0.0                 | 0.00          | 1.00                   | 1.00           | 0.00045                  | 0.87 |
| 0.3% Cu/HAP       | 5.8                  | 23.1                  | 0.3                 | 0.285         | 8                      | 100            | 0.56                     | 0.98 |
| 0.5% Cu/HAP       | 6.1                  | 23.2                  | 0.5                 | 0.475         | 7                      | 100            | 0.63                     | 0.97 |
| 0.7% Cu/HAP       | 9.6                  | 26.5                  | 0.7                 | 0.665         | 6                      | 100            | 0.71                     | 0.93 |
| 1% Cu/HAP         | 8.6                  | 26.5                  | 1.0                 | 0.950         | 8                      | 100            | 0.46                     | 0.99 |

Table 1. Specific Surface Area, Crystallite Size, Theoretical and Actual Cu Contents, Time of Completion of the Reaction, Catalytic Efficiency, Apparent Rate Constant, and $R^2$ of the Pure 1D HAP and Cu/HAP Nanocomposites.

Figure 3. XPS spectra of the pure 1D HAP and 0.7% Cu/HAP nanocomposite: (a) full survey spectra, (b) Ca 2p spectrum, (c) P 2p spectrum, (d) O 1s spectrum, (e) C 1s spectrum, and (f) Cu 2p spectrum.
shifted to 290.5 and 287.2 eV, respectively, in the 0.7% Cu/HAP nanocomposite. The Cu 2p's high-resolution spectrum (Figure 3f) revealed two peaks with the bonding energy values of 932.1 eV (Cu 2p_{3/2}) and 952.1 eV (Cu 2p_{1/2}), which were characteristic for zero-valent Cu.  

Figure 4 shows the TEM and the high-resolution transmission electron microscopy (HR-TEM) micrographs of the 0.7% Cu/HAP nanocomposite. The nanocomposite constituted of a rod-like shape with an average length of ~308 nm and an average width of ~117 nm. The HR-TEM image of this nanocomposite (Figure 4b) showed the crystalline phase of HAP with well-resolved lattice fringes. The distances between the adjacent lattices fringes (0.27 nm) were ascribed to the adjacent (112) plane of HAP NPs. Unfortunately, the Cu NPs cannot be observed on the surface of the 1D HAP support by TEM, which may be due to the low contrast between Cu particles and the HAP support. Figure 5a–f shows the elemental distribution that is present in the 0.7% Cu/HAP nanocomposite. The elemental mapping of Cu, Ca, P, and O through EDX area scanning indicates that the distribution of various elements is uniform. EDX also confirms the successful assembly of Cu NPs onto the HAP support.

### 3.2. Catalytic Reduction of 4-NP

At an ambient temperature, the catalytic activity of the 1D HAP and Cu/HAP nanocomposites was examined using a model reduction reaction of 4-NP to 4-AP in the presence of excess amounts of NaBH₄. The UV–vis peak of a pure 4-NP aqueous solution is 317 nm, which shifts to around 400 nm when NaBH₄ is added, leading to the formation of 4-nitrophenolate (4-NPL) anions in an alkaline medium. Moreover, the mixture color turned from faint yellow to intense yellow. The 4-NPL absorption peak (400 nm) and the mixture color were fitted with a linear function (Figure 6c). The rate constant values were estimated from the slopes of the linear lines. The obtained k_{app} values are 0.00045 and 0.56 min⁻¹ for the pure 1D HAP and 0.3% Cu/HAP nanocomposite-catalyzed 4-NP, respectively. The high dispersion of Cu NPs on the 1D HAP surface and a high specific surface area, which promotes rapid electron transfer from NaBH₄ to 4-NP, is largely responsible for the composite’s improved catalytic activity.

The turnover frequency (TOF, mmol mg⁻¹ s⁻¹) value was estimated using eq 3 to further evaluate the catalytic activity:

\[
\frac{\ln A_t}{A_0} = -k_{app} t
\]

where A_t and A_0, respectively, denote the absorption peak intensities of 4-NPL (400 nm) at time t = t and t = 0 and k_{app} is the apparent rate constant of the reaction.

To evaluate the reaction’s rate constants using 1D HAP and 0.3% Cu/HAP, ln(A_t/A_0) is plotted against time, and the data were fitted with a linear function (Figure 6c). The rate constant values were estimated using the pseudo-first-order kinetic model on the UV–vis absorption spectra collected at various time intervals. The following equation was used to calculate the reduction rate of 4-NP

\[
\ln \frac{A_t}{A_0} = -k_{app} t
\]
where \( N_{\text{4NP}} \) is the 4-NP concentration in mmol, \( M_{\text{CuNPs}} \) is the exact amount of Cu NPs in milligram that was present in 1 mg of the Cu NP/HAP catalyst, and \( t \) is the reaction time. The TOF was calculated to be \(7.4 \times 10^{-6}\) mmol mg\(^{-1}\) s\(^{-1}\) for the 0.3% Cu/HAP nanocomposite.

3.2.1. Effect of Copper Content. The time of completion of 4-NP reduction, the \( k_{\text{app}} \) values, and the \( R^2 \) values for the different composites containing different amounts of Cu NPs are presented in Table 1. It was found that the reaction completes quicker upon increasing the Cu NP contents in the composite. The catalytic activity of the 0.7% Cu/HAP nanocomposite was higher than 0.3% Cu/HAP, 0.5% Cu/HAP, and 1% Cu/HAP nanocomposites. The apparent reaction rate constants of Cu/HAP nanocomposite catalysts with different Cu NP contents were calculated to be 0.56 min\(^{-1}\) (0.3% Cu/HAP), 0.63 min\(^{-1}\) (0.5% Cu/HAP), 0.71 min\(^{-1}\) (0.7% Cu/HAP), and 0.46 min\(^{-1}\) (1% Cu/HAP). These findings demonstrated that 0.7% Cu/HAP exhibits better activity in the 4-NP reduction, when compared to the other three composites. The 0.7% Cu/HAP nanocomposite has a higher surface area than the other catalysts, allowing for more active catalytic sites, and this catalyst was chosen for further studies. The aggregation of Cu NPs on the surface of 1D HAP may be the cause of the observed decrease in the catalytic efficiency of the 1% Cu/HAP nanocomposite.

3.2.2. Effect of Catalyst Weight. In Figure 7, the catalytic activity is examined as a function of the 0.7% Cu/HAP catalyst weight with the initial concentration of 4-NP at 0.1 mM, NaBH\(_4\) concentration at 0.1 M, and 100 mL of reaction mixture. The apparent reaction rate constant increases as the catalyst weight increases, with 30 mg being the ideal catalyst weight. This is due to an increase in the active catalytic sites, which allows for a large transfer of 4-NP and BH\(_4\)\(^{-}\) onto the surface of the 0.7% Cu/HAP nanocomposite.

3.2.3. Mechanism of Reduction of 4-NP. The 4-NP reduction over the Cu/HAP nanocomposite is an electron-transfer process and proceeded through two steps. The first step included the diffusion of BH\(_4\)\(^{-}\) and 4-NP from the aqueous solution and absorbance on the Cu NPs via \(\pi-\pi\) stacking interactions.\(^{47}\) The second step involved employing Cu NPs on the surface of 1D HAP as an electron mediator to transport electrons from BH\(_4\)\(^{-}\) to 4-NP. The hydrogen produced by BH\(_4\)\(^{-}\) attacks the 4-NP molecule, reducing it, and the product (4-AP) is desorbed off the catalyst’s surface. From the above mechanism, it can deduce that 1D HAP can prevent Cu NPs from aggregating, while also improving the catalytic efficiency through a synergistic effect.

3.2.4. Catalyst Reusability. For the actual applications, reusability and stability are the key features of the catalyst. The 0.7% Cu/HAP nanocomposite was used for five consecutive cycles, and the results are displayed in Figure 8. After the first cycle, the composite was isolated from the reaction mixture by centrifugation and cleaned several times by bi-distilled water and ethanol. The collected composite was dried for 2 h at 90 °C and reused for the reduction of fresh 4-NP solution, where the same conditions are used as in the first cycle. The activity parameter (\(K\)) of the most active nanocomposite (0.7% Cu/HAP) was calculated for quantitative comparison, which is known as the ratio of \(k_{\text{app}}\) to the weight of the catalyst\(^{48}\) or to the weight of the active species\(^{49-51}\) used. It can be estimated by two equations as follows.
\[ K_1 = \frac{k_{\text{app}}}{m_T} \]  

\[ K_2 = \frac{k_{\text{app}}}{m_M} \]

where \( m_T \) represents the total mass of the catalyst used and \( m_M \) is the weight of the active metal species in the catalyst used in the reaction. The \( k_{\text{app}} \), \( K_1 \), and \( K_2 \) values for the 0.7% Cu/HAP nanocomposite in the reduction of 4-NP were compared to those of previously reported catalysts in the literature (Table 2). The result revealed that the 0.7% Cu/HAP nanocomposite has higher \( k_{\text{app}} \) and \( K_2 \) values than the other catalysts. Because of the high specific surface area, doping effect, ultrafine size, and good dispersion of Cu NPs, this nanocomposite has a high catalytic activity.

### 3.3. Catalytic Reduction of the Organic Dye

#### 3.3.1. Congo Red (CR) Reduction

At an ambient temperature
and in an aqueous medium, the reduction of CR (anionic dye), when there is an excess of NaBH₄, was utilized as a model reaction to verify the catalytic activity of the most active composite (0.7% Cu/HAP). In an aqueous solution, CR showed two bands at 350 and 498 nm, which are characteristic to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. When there is NaBH₄ only, no considerable change in the peak’s intensities and the color of CR was observed for a long time. In a typical experiment, 0.05 mM CR, 0.1 M NaBH₄, 100 mL of reaction mixture, and 30 mg of 0.7% Cu/HAP nanocomposite were used. The color and peak intensities of the CR dye rapidly declined with time after the composite was added to the dye and NaBH₄ mixture, and the red color completely disappeared after ~4 min (Figure 9a). In addition, a new peak at 290 nm evolved with time. As with 4-NP reduction, the reduction reaction followed a pseudo-first-order kinetic pathway. The slope of the linear plot of $\ln \left( \frac{A_t}{A_0} \right)$ versus time (Figure 9c) was used to obtain the $k_{app}$ value, which was found to be equal to 0.95 min⁻¹.

### 3.3.2. ACF Reduction

The reduction of ACF (fluorescent dye) in the presence of excess amount of NaBH₄ was also chosen to estimate the activity of the 0.7% Cu/HAP nanocomposite, and the data are displayed in Figure 9b. The aqueous solution of ACF exhibits an absorption band at 450 nm, and in this work, the reduction of ACF was monitored at 450 nm.

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### Table 2. Comparison of the Activity of the Most Active Catalyst (0.7% Cu/HAP Nanocomposite) with Other Catalysts That Are Published in the Literature.

| catalysts                  | reaction conditions                          | efficiency (%) | time (s) | $k_{app}$ (s⁻¹) | $k_1$ (g⁻¹ s⁻¹) | $k_2$ (g⁻¹ s⁻¹) | Ref.   |
|---------------------------|---------------------------------------------|----------------|----------|----------------|----------------|----------------|--------|
| Cu/HAP/ZnFe₂O₄ Cat. (10 mg), 4-NP (0.071 mM), NaBH₄ (0.01 M) | 100 | 5 | | | | | 21 |
| Ag@mHAp-Si-(S) Cat. (2 mg), 4-NP (0.66 M), NaBH₄ (1 M) | 93 | 120 | 0.02500 | 12.5 | 178.3 | | 19 |
| Ag decorated HAP Cat. (2 mg), 4-NP (0.09 mM), NaBH₄ (0.018 M) | 100 | 300 | 0.00730 | 3.65 | 10.42 | | 20 |
| Ag/HAP Cat. (2 mg), 4-NP (0.072 mM), NaBH₄ (5.2 mM) | 100 | 300 | 0.01133 | 5.66 | 302.9 | | 22 |
| Apatite@Au Cat. (1 mg), 4-NP (0.125 mM), NaBH₄ (0.05 mM) | | | 0.00030 | 0.3 | 0.333 | | 52 |
| Cu−COF Cat. (1 mg/mL), 4-NP (0.133 mM), NaBH₄ (19.6 mM) | 100 | 960 | 0.00470 | | | | 24 |
| Cu₅₅ Cat. | | | 0.03340 | | | | 25 |
| CNT/PEI2-Cu Cat. (−), 4-NP (200 mg L⁻¹), NaBH₄ (0.1 M) | 100 | 2700 | 0.01283 | | | | 26 |
| Cu−Cu₅ Cat. (0.025 mg), 4-NP (0.154 mM), NaBH₄ (0.005 M) | 98.9 | 420 | 0.00246 | 98.4 | 98.40 | | 27 |
| Cu−SG HCO₃⁻ Cat. (10 mg), 4-NP (0.1 mM), NaBH₄ (0.03 M) | 99.1 | 180 | 0.02713 | 2.71 | 19.70 | | 29 |
| Cu−ICAI Cat. (−), 4-NP (0.2 mM), NaBH₄ (5 mM) | 100 | 90 | 0.07283 | | | | 30 |
| Cu−BNO Cat. (5 mg), 4-NP (0.16 mM), NaBH₄ (0.008 M) | 100 | 300 | 0.01153 | 2.3 | | | 31 |
| Ag₉₅−Cu₅₅, NPs@PZS Cat. (0.1 mg), 4-NP (0.066 mM), NaBH₄ (2.8 mM) | 100 | 300 | 0.00893 | 89.3 | | | 32 |
| Cu@SiO₂−Cl−Ni/700 Cat. (0.2 mg), 4-NP (0.1 mM), NaBH₄ (26.4 mM) | 100 | 450 | 0.00931 | 46.5 | 51.0 | | 51 |
| 0.7% Cu/HAP Cat. (30 mg), 4-NP (0.1 mM), NaBH₄ (0.1 M) | 100 | 60 | 0.108 | 3.6 | 541.3 | | this work |

**Figure 9.** UV−vis spectra of reduction of (a) CR and (b) ACF dye and (c) plots of $\ln \left( \frac{A_t}{A_0} \right)$ vs reaction time in the presence of 0.7% Cu/HAP nanocomposite as a catalyst.
nm. The color and the peak intensity of the ACF solution did not change by the addition of NaBH₄ within 1 h in the typical reduction conditions: 0.1 mM ACF, 0.1 M NaBH₄, 100 mL of reaction mixture, and 30 mg of 0.7% Cu/HAP nanocomposite. After the addition of the composite to the reaction mixture, the color and the peak intensity of ACF completely disappeared within 2 min. As NaBH₄ present in the reaction in excess, thus, the reaction also obeyed the pseudo-first-order kinetics equation. From the slope of the linear plot of ln(Aₒ/Aₜ) versus time (Figure 9c), the $k_{app}$ value was calculated to be 3.19 min⁻¹.

4. CONCLUSIONS

Metallic Cu NPs were doped 1D HAP by a facile chemical reduction method by ascorbic acid as a reducing agent. The crystallinity and the specific surface area increased by increasing the Cu NP content. The XPS and EDX techniques confirmed the successful assembly of metallic Cu NPs and uniformly distributed onto HAP. At room temperature, the produced nanocomposites showed good catalytic efficiency in the reduction of 4-NP in the presence of NaBH₄. The 0.7% Cu/HAP nanocomposite showed the highest catalytic performance, and it can reduce 4-NP in ~1 min, with a good recyclability. The excellent catalytic activity of this nanocomposite can be attributed to the uniform dispersion of Cu NPs on the HAP surface, large specific surface area, and the one-dimensional structure of the support. The synthetic procedure of the Cu/HAP nanocomposites is very cheap and simple, and their catalytic activity for the organic pollutants reduction in water is surprising; as a result, this study points to a promising path for the creation of novel nanocomposite catalysts.

DATA AVAILABILITY

All data generated or analyzed during this study are included in this published article.

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Abdelhafeez, I. A.; El-Tohamy, S. A.; ul-Malik, M. A.; Abdel-Raheem, S. A. A.; El-Dar, F. M. S. A Review on Green Remediation Techniques for Hydrocarbons and Heavy Metals Contaminated Soil. Curr. Chem. Lett. 2022, 11, 43–62.
(2) Marimuthu, M.; Li, H.; Chen, Q. Facile Ultrasonic Synthesis of Silver-Based Bimetal Nanoparticles for Efficient Catalytic Reduction of 4-Nitrophenol. J. Mol. Liq. 2021, 333, 115963.
(3) Zhang, X.-Q.; Shen, R.-F.; Guo, X.-J.; Yan, X.; Chen, Y.; Hu, J.-T.; Lang, W. Bimetallic Ag-Cu Nanoparticles Anchored on Polypropylene (PP) Nonwoven Fabrics: Superb Catalytic Efficiency and Stability in 4-Nitrophenol Reduction. Chem. Eng. J. 2021, 408, 128018.
(4) Rasaki, S. A.; Zhao, C.; Wang, R.; Wang, J.; Jiang, H.; Yang, M. Facile Synthesis Approach for Preparation of Robust and Recyclable Ag/ZnO Nanorods with High Catalytic Activity for 4-Nitrophenol Reduction. Mol. Catal. 2021, 504, 111433.
(5) Paul, D.; Sachan, D.; Das, G. Silver Nanoparticles Embedded on In-Vitro Biomineralyzed Vaterite: A Highly Efficient Catalyst with Enhanced Catalytic Activity towards 4-Nitrophenol Reduction. Mol. Catal. 2021, 504, 111433.
(6) Yang, T.; Tang, Y.; Liu, L.; Gao, Y.; Zhang, Y. Cu-Anchored CNTs for Effectively Catalytic Reduction of 4-Nitrophenol. Chem. Phys. 2020, 533, 110738.
(7) Zhang, M.; Su, X.; Ma, L.; Khan, A.; Wang, L.; Wang, J.; Maloletnev, A. S.; Yang, C. Promotion Effects of Halloysite Nanotubes on Catalytic Activity of Co3O4 Nanoparticles toward Reduction of 4-Nitrophenol and Organic Dyes. J. Hazard. Mater. 2021, 403, 123870.
(8) Tan, X.; Qin, J.; Li, Y.; Zeng, Y.; Zheng, G.; Feng, F.; Li, H. Self-Supporting Hierarchical PdCu Aerogels for Enhanced Catalytic Reduction of 4-Nitrophenol. J. Hazard. Mater. 2020, 397, 122786.
(9) Ratima, R.; Unnikrishnan, G. Porous Poly(Lactic Acid)/Nano-Silver Composite Membranes for Catalytic Reduction of 4-Nitrophenol. Mater. Chem. Phys. 2020, 241, 122389.
(10) Hira, S. A.; Hui, H. S.; Yusuf, M.; Park, K. H. Silver Nanoparticles Deposited on Metal Tungsten Bronze as a Reusable Catalyst for the Highly Efficient Catalytic Hydrogenation/Reduction of 4-Nitrophenol. Catal. Commun. 2020, 141, 106011.
(11) Li, Q.; Song, H.; Ye, Y.; Pan, F.; Zhang, D.; Xia, D. A Green Designed Copper-Resin Composite for Highly Efficient Catalytic Reduction of 4-Nitrophenol. Colloid Interface Sci. Commun. 2021, 42, 100407.
(12) Nasrollahzadeh, M.; Majadi, S. M.; Rostami-Vartooni, A.; Bagherzadeh, M.; Safari, R. Immobilization of Copper Nanoparticles on Perlite: Green Synthesis, Characterization and Catalytic Activity on Aqueous Reduction of 4-Nitrophenol. J. Mol. Catal. A: Chem. 2015, 400, 22–30.
(13) Hang, L.; Zhao, Y.; Zhang, H.; Liu, G.; Cai, W.; Li, Y.; Qi, L. Copper Nanoparticle@graphene Composite Arrays and Their Enhanced Catalytic Performance. Acta Mater. 2016, 105, 59–67.
(14) Xie, Y.; Liu, B.; Li, Y.; Chen, Z.; Cao, Y.; Jia, D. Cu/Cu2O/RGO Nanocomposites: Solid-State Self-Reduction Synthesis and Catalytic Activity for p-Nitrophenol Reduction. New J. Chem. 2019, 43, 12118–12123.
(15) Liu, W.-J.; Tian, K.; Jiang, H.; Yu, H.-Q. Harvest of Cu NP Anchored Magnetic Carbon Materials from Fe/Cu Preloaded Biomass: Their Pyrolysis, Characterization, and Catalytic Activity on Aqueous Reduction of 4-Nitrophenol. Green Chem. 2014, 16, 4198–4205.
(16) Chen, G.; Shan, R.; Shi, J.; Liu, C.; Yan, B. Biodiesel Production from Palm Oil Using Active and Stable K Doped Hydroxyapatite Catalysts. Energy Convers. Manage. 2015, 98, 463–469.
(17) Çelik, D.; Karahan, S.; Zähmakanir, M.; Özkär, S. Hydrogen Generation from the Hydrolysis of Hydrate-Borane Catalyzed by
Rhodium(0) Nanoparticles Supported on Hydroxyapatite. Int. J. Hydrogen Energy 2012, 37, 5143−5151.

(18) Kamienski, J.; Kelly, P. J.; Banks, C. E.; Doyle, A. M. Methane Emission Management in a Dual-Fuel Engine Exhaust Using Pd and Ni Hydroxyapatite Catalysts. Fuel 2017, 208, 314−320.

(19) Bahadorikhalili, S.; Arshadi, H.; Afrouzandeh, Z.; Ma’mani, L. Ultrasonic Promoted Synthesis of Ag Nanoparticle Decorated Thiourea-Functionalized Magnetic Hydroxyapatite: A Robust Inorganic–Organic Hybrid Nanocatalyst for Oxidation and Reduction Reactions. New J. Chem. 2020, 44, 8840−8848.

(20) Das, T. K.; Ganguly, S.; Bhawal, P.; Mondal, S.; Das, N. C. A Facile Green Synthesis of Silver Nanoparticle-Decorated Hydroxyapatite for Efficient Catalytic Activity towards 4-Nitrophenol Reduction. Res. Chem. Intermed. 2018, 44, 1189−1208.

(21) Das, K. C.; Dhar, S. S. Fast Catalytic Reduction of P-Nitrophenol by Cu/HAP/ZnFe2O4 Nanocomposite. Mater. Sci. Eng., B 2021, 263, 114841.

(22) Hoang, T. T. T.; Insin, N.; Sukpriom, N. Catalytic Activity of Silver Nanoparticles Anchored on Layered Double Hydroxides and Hydroxyapatite. Inorg. Chem. Commun. 2020, 121, 108199.

(23) Xiong, Z.-C.; Yang, Z.-Y.; Zhu, Y.-J.; Chen, F.-F.; Yang, R.-L.; Qin, D.-D. Ultralong Hydroxyapatite Nanowire-Based Layered Catalytic Paper for Highly Efficient Continuous Flow Reactions. J. Mater. Chem. A 2018, 6, 5762−5773.

(24) Wu, Z.; Zhu, J.; Wen, W.; Zhang, X.; Wang, S. Spherical Covalent Organic Framework Supported Cu/Ag Bimetallic Nanoparticles with Highly Catalytic Activity for Reduction of 4-Nitrophenol. J. Solid State Chem. 2022, 217, 123116.

(25) Matinise, N.; Khutlane, J. T.; Malgas-Enus, R. The Effect of Magic Number Phosphine Stabilised Mono- and Bimetallic Au, Cu and Au-Cu Nanoparticles as Catalysts in the Reduction of 4-Nitrophenol—A Kinetic Study. Nano-Struct. Nano-Objects 2022, 29, 100814.

(26) Oh, S.; Yu, H.; Han, Y.; Jeong, H. S.; Hong, H.-J. 3-D Porous Cellulose Nanofibrill Aerogels with a Controllable Copper Nanoparticle Loading as a Highly Efficient Non-Noble-Metal Catalyst for 4-Nitrophenol Reduction. Chemosphere 2022, 301, 134518.

(27) Verma, A.; Anand, P.; Kumar, S.; Fu, Y.-P. Cu-Cuprous/Cupric Oxide Nanoparticles towards Dual Application for Nitrophenol Conversion and Electrochemical Hydrogen Evolution. Appl. Surf. Sci. 2022, 578, 151795.

(28) Locatelli, P. F. F.; Gurtat, M.; Lens, G. F.; Marroquin, J. F. R.; Pellegrini, F.; Schneider, R.; Borba, C. E. Simple Borophosphate Glasses for On-Demand Growth of Self-Supported Copper Nanoparticles in the Reduction of 4-Nitrophenol. J. Hazard. Mater. 2021, 416, 125801.

(29) Dan, H.; Song, Y.; Xu, Y.; Gao, Y.; Kong, W.; Huang, Y.; Yue, Q.; Gao, B. Green Synthesis of Cu Nanoparticles Supported on Straw-Graphene Composite for Catalytic Reduction of p-Nitrophenol. J. Cleaner Prod. 2021, 283, 124578.

(30) Sun, J.; Li, M.; Sun, X.; Wang, L.; Han, P.; Qi, G.; Gao, D.; Zhang, L.; Tao, S. Copper-Based Integral Catalytic Impeller for the Rapid Catalytic Reduction of 4-Nitrophenol. ACS Omega 2021, 6, 21784−21791.

(31) Jiang, X.; Han, B.; Zhou, C.; Xia, K.; Gao, Q.; Wu, J. Cu Nanoparticles Supported on Oxygen-Rich Boron Nitride for the Reduction of 4-Nitrophenol. ACS Appl. Nano Mater. 2018, 1, 6692−6700.

(32) Ahmad, M.; Nawaz, T.; Assiri, M. A.; Hussain, R.; Hussain, I.; Imran, M.; Ali, S.; Wu, Z. Fabrication of Bimetallic Cu–Ag Nanoparticle-Decorated Poly(Cyclotriphosphazene-Co-4,4′-Sulfonyldiphenol) and Its Enhanced Catalytic Activity for the Reduction of 4-Nitrophenol. ACS Omega 2022, 7, 7096−7102.

(33) Ali, H. M.; Ibrahim, S. M.; Abo Zeid, E. F.; Al-Hossainy, A. F.; El-Aal, M. A. A Comparative Study of Cu-Anchored 0D and 1D ZnO Nanostructures for the Reduction of Organic Pollutants in Water. RSC Adv. 2022, 12, 16496−16509.

(34) Gopi, D.; Indira, J.; Nithiya, S.; Kavitha, L.; Mudali, U. K.; Kanimozi, K. Influence of Surfactant Concentration on Nano-hydroxyapatite Growth. Bull. Mater. Sci. 2013, 36, 799−805.
(52) Wang, T.; Yao, Y.; Wei, A.; Jia, L.; Chen, S. Facile Synthesis, Microstructure, and Photo-Catalytic Activity of Novel Flower-like Apatite@Au Composite Nanosheet Spheres. *Mater. Lett.* **2018**, *220*, 129–132.

(53) Ganapuram, B. R.; Alle, M.; Dadigala, R.; Dasari, A.; Maragoni, V.; Guttena, V. Catalytic Reduction of Methylene Blue and Congo Red Dyes Using Green Synthesized Gold Nanoparticles Capped by Salmalia Malabarica Gum. *Int. Nano Lett.* **2015**, *5*, 215–222.