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Research Article

Synthesis and Investigation of Antimicrobial Activity of Cu_2O Nanoparticles/Zeolite

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Cuprous oxide (Cu_2O) nanoparticles in zeolite A were synthesized by two steps: (i) ion-exchange of copper ions into the zeolite and (ii) reduction of copper ions in cages of the zeolite by hydrazine hydrate in base medium. The Cu_2O nanoparticles/zeolite product was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDX). The particle size of Cu_2O nanoparticles was of 40 nm. The antibacterial activity of the as-synthesized Cu_2O nanoparticles/zeolite against *Escherichia coli* was also investigated. Cu_2O NPs/zeolite product can be favorably produced on large scale for water treatment and agricultural application as antimicrobial agent.

1. Introduction

Metal nanoparticles (NPs) have attracted considerable attention because of their unique properties such as catalytic, magnetic, optical, biological, and electrical properties. Among metal NPs, Au and Ag NPs have been most extensively studied and applied due to their stability and suitability to handle in air [1]. Recently, Cu NPs have been expected to be a good choice of the next-generation NPs mainly because of low cost [2]. In addition, Cu oxide NPs, namely, cupric oxide (CuO) and cuprous oxide (Cu_2O), are among the most widely used as antimicrobial agents for their high efficacy towards a broad spectrum of microorganisms [2–4]. There has been also considerable attention throughout the years for Cu_2O as a candidate material for photovoltaics, photocatalytic degradation of organic pollutants and decomposition of water into O_2 and H_2 under visible light, and even as a negative electrode material for lithium ion batteries [5–7]. According to Wick and Tilley [8], Cu_2O is a promising material with the capacity for low cost, large-scale solar energy conversion due to the abundant nature of copper and oxygen, suitable bandgap of visible light, and effective, low energy intensity fabrication process. The antimicrobial activity of copper has long been recognized. However, relatively few studies have been focused on the antimicrobial properties of Cu oxide NPs [4]. Huang et al. [3] reported that the inhibition efficiency of the 500–750 mg/kg CuO NPs against tomato early blight *A. solani* was 70.7–80.7%; it is better than that of the 50% carbendazim. Furthermore, the inhibition effect of the 500 mg/kg CuO NPs on pepper root rot pathogen was significantly lower than that of the 75% chlorothalonil but higher than that of the 50% carbendazim. However, the CuO NPs showed no inhibitory effect on vegetable *B. cinerea* pathogen. According to Ren et al. [9], both octahedral and cubic Cu_2O crystals could inhibit the growth of *E. coli* efficiently, and their bactericidal activities become stronger with increased Cu_2O concentration. Up to 85% *E. coli* are killed in the presence of Cu_2O particles with concentration of 25 μ/mL. Zeolite A is microporous aluminosilicate material with small pore size and high absorptivity commonly used as a commercial adsorbent in gas purification and ion-exchange separation [10]. Zeolite A is also used as catalyst, as molecular sieve, in the production of laundry detergents, in agriculture purposes for the preparation of advanced materials and recently to produce the nanocomposites [11]. Synthesis of CuO NPs within zeolite Y by reaction of Cu^{2+}-exchanged zeolite with

sodium hydroxide and calcification at 350°C for 2 h was studied by Razavi and Loghman-Estarki [12]. In the present study, Cu_2O NPs were synthesized within the zeolite A framework using $CuSO_4$ as copper precursor and hydrazine hydrate ($N_2H_4{\cdot}H_2O$) as reducing agent. The antibacterial activity of the obtained Cu_2O NPs/zeolite against *Escherichia coli* (*E. coli*) was also investigated.

2. Methods

2.1. Materials and Chemicals. Analytical grade $CuSO_4{\cdot}5H_2O$, NH_4OH (25%), and $N_2H_4{\cdot}H_2O$ (80%) were products from Merck, and industrial grade sodium type of zeolite A with chemical formulation $Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}4.5H_2O$ was a product from Shangdong Aluminium Corporation (SALCO, China). The Luria-Bertani (LB) medium for bacterial incubation was purchased from Himedia, India. The strain of *E. coli* ATCC 6538 was provided by the University of Medical Pharmacy, Ho Chi Minh City. Distilled water was used in all experiments.

2.2. Exchange of Cu^{2+} Ions in Zeolite. 1 kg of zeolite was suspended into a glass beaker containing 1.5 L water. Then, HNO_3 2 N and water were added to zeolite suspension mixture for neutralization to pH ~6.5 and for final volume of about 4 L. 0.42 kg of $CuSO_4{\cdot}5H_2O$ was dissolved in 500 mL water and then poured slowly into neutralized zeolite suspension mixture. Stirring was carried out for 2 h at ambient temperature for complete exchange of Cu^{2+} into zeolite. Before adding hydrazine, pH of the Cu^{2+}/zeolite mixture was adjusted by ammonia water to ~7.5.

2.3. Reduction of Cu^{2+} to Cu_2O NPs in Zeolite. A freshly prepared 250 mL hydrazine 20% (w/v) solution was added dropwise to the above Cu^{2+}/zeolite under stirring for 2 h at ambient temperature. Then, reduction reaction was stopped and let standing overnight for Cu_2O NPs/zeolite settling down. Finally, Cu_2O NPs/zeolite product was filtered off using cotton fabric, washed several times with water, and dried in a forced air oven at 60°C till to constant weight.

2.4. Characterization of Cu_2O NPs/Zeolite. The content of copper in Cu_2O NPs/zeolite product was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Perkin-Elmer, Optima 5300 DV. X-ray diffraction (XRD) of Cu_2O NPs/zeolite product was carried out on D8 Advance Bruker, Germany, and the Cu_2O NPs sizes were measured using a transmission electron microscope (TEM; JEM 1010, JEOL, Tokyo, Japan). The presence of copper in Cu_2O NPs/zeolite was also assessed by energy-dispersive X-ray spectroscopy (EDX) on a JEOL 6610 LA.

2.5. Antibacterial Activity of Cu_2O NPs/Zeolite. In vitro test of bactericidal activity of Cu^{2+}/zeolite and Cu_2O NPs/zeolite against *E. coli* was carried out following the procedure as described in [13–15]. Briefly, the antibacterial activity of the materials was tested by culture medium toxicity method in Luria-Bertani medium. The test material samples and control were shaken in *E. coli* suspension at 150 rpm at room temperature for 4 h. After that, the number of viable bacteria in each mixture was determined by spread plate technique on LB agar plates. The antibacterial efficiency (η) was calculated using the equation: $\eta\,(\%) = (N_o - N) \times 100/N_o$, where N_o and N are the survival numbers of bacteria in the control and studied samples, respectively.

3. Results and Discussion

3.1. Characterization of Cu_2O NPs/Zeolite. Figure 1 showed the photograph of zeolite, Cu^{2+}/zeolite, and Cu_2O NPs/zeolite. It is clearly observed from Figure 1 that Cu_2O NPs/zeolite is reddish color. The reaction of hydrazine used as reducing agent can be expressed by

$$N_2H_4 + 4OH^- \longrightarrow N_2 + 4H_2O + 4e^- \quad (1)$$

Dimitrijević et al. reported that hydrazine hydrate has been considered as a preferred reducing agent and used for industrial scale production of silver powder for decades [16]. According to Kuo and Huang [17], in base medium the formation of Cu_2O NPs can be described in the following reactions:

$$2Cu\,(OH)_4^{2-} + N_2H_4 + 2OH^- \longrightarrow Cu_2O + N_2 + 5H_2O + 4OH^- \quad (2)$$

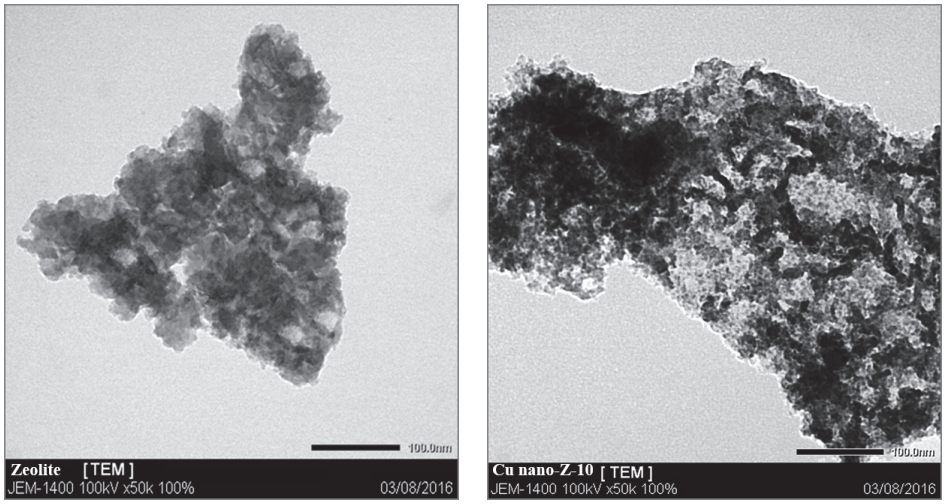
$$Cu_2O + Cu_2O + Cu_2O + \cdots \longrightarrow Cu_2O \text{ nano} \quad (3)$$

TEM images of zeolite and Cu_2O NPs/zeolite in Figure 2 indicated that the size of Cu_2O NPs in the frameworks of the zeolite was in the range from 5 to about 30 nm. It can be also surprisingly observed in Figure 2 that, beside the black dots, some parts of the morphology of Cu_2O NPs in zeolite were almost as wormlike form. These Cu_2O NPs seem to be linked together within the intercages of zeolite structure.

The XRD pattern of Cu_2O NPs/zeolite A in Figure 3 showed that diffraction peaks appeared at 29.61°, 36.48°, 42.38°, 61.46°, 73.56°, and 77.52° corresponding to (110), (111), (200), (220), (311), and (222) planes of cuprite, respectively, that indicated the formation of Cu_2O nanocrystals (JCPDS Card number 05-0667) [4, 18]. The average crystalline size of Cu_2O NPs determined by taking the full width at half maximum (FWHM) of the most intense peak at 36.48° using Debye-Scherrer's formula [18] was of about 40 nm. The crystalline size calculated from XRD patterns is usually bigger than that from TEM images that also happened in our previous study [14] and in this study as well. There was not any diffraction peak in XRD pattern in Figure 3 assigned for CuO nanocrystal; however, low intensity peaks also appeared at 43.36°, 50.43°, and 74.25° that assigned for Cu nanocrystals (JCPDS Card number 04-0836) [4, 12]. Thus, during reduction reactions, a certain small amount of Cu could be formed in the following reaction:

$$2Cu^{2+} + N_2H_4 + 4OH^- \longrightarrow 2Cu^{o} + N_2 + 4H_2O \quad (4)$$

Figure 1: Photograph of zeolite (a), Cu^{2+}/zeolite (b), and Cu_2O NPs/zeolite (c).



(a) (b)

Figure 2: TEM images of zeolite A (a) and Cu_2O NPs/zeolite A (b).

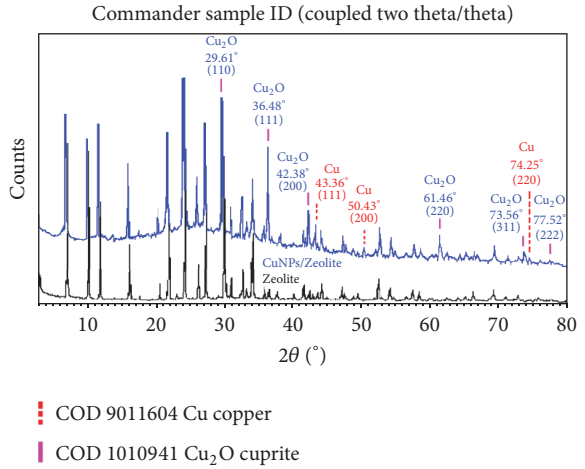


Figure 3: XRD patterns of zeolite A and Cu_2O NPs/zeolite A.

According to Giannousi et al. [4] and Xia et al. [19], Cu_2O should be also formed due to the disproportionation reaction of Cu and Cu^{2+}:

$$Cu^{o} + Cu^{++} + 2OH^{-} \longrightarrow Cu_2O + H_2O \quad (5)$$

It seems that not all resultant Cu reacts with Cu^{2+}. So that small trace of Cu crystal could be contained in the Cu_2O NPs/zeolite product as presented in XRD pattern in Figure 3. Khan et al. [18] also reported that the color of the Cu-Cu_2O NPs mixture was dark yellowish that was different from black color of CuO [20] and reddish color (or brick color) of Cu_2O (Figure 1). According to Arshadi-Rastabi et al. [21], Cu_2O NPs have various ranges of different colors, namely, yellow, orange, red, and brown color.

The energy-dispersive X-ray (EDX) spectra in Figure 4 showed that the composition of zeolite A consists of four

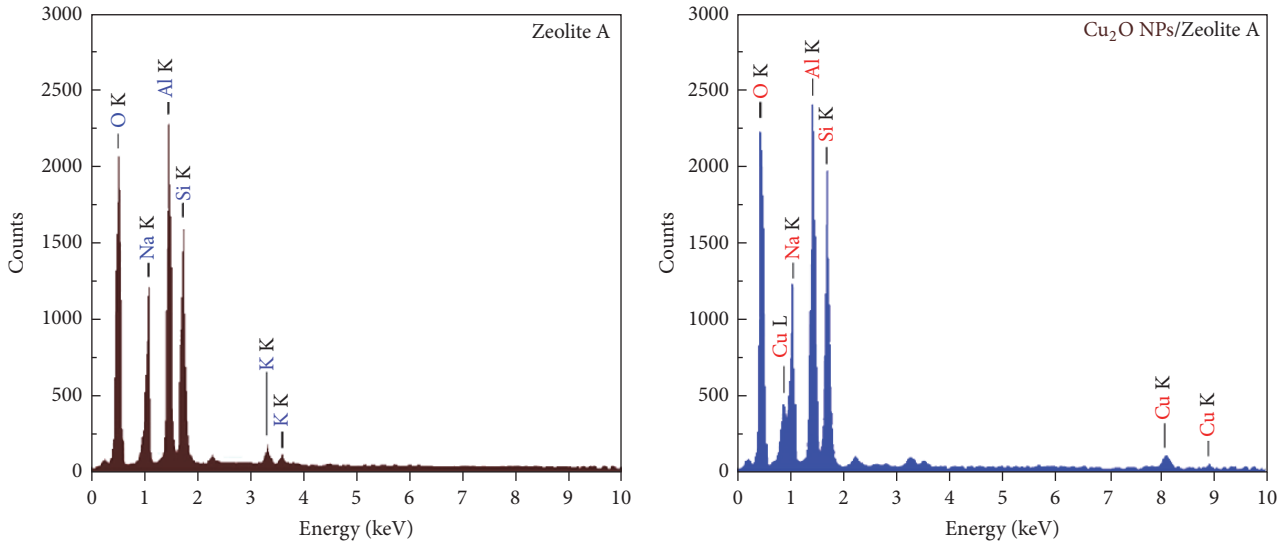


FIGURE 4: EDX spectra of zeolite and Cu_2O NPs/zeolite.

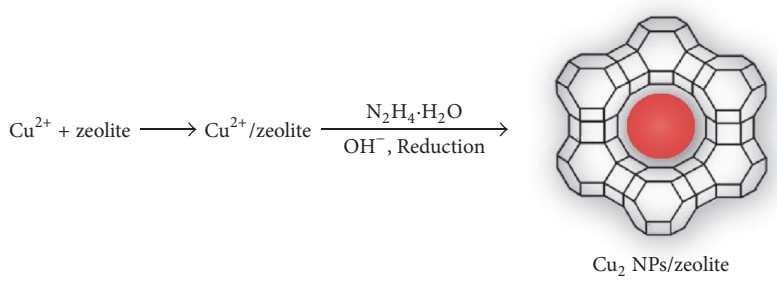


FIGURE 5: Brief schematic diagram of Cu_2O NPs/zeolite synthesis procedures.

main elements, particularly silicon, aluminum, oxygen, sodium, and a small amount of potassium, but without any trace of copper. After exchange with Cu^{2+} and reduction of Cu^{2+} to Cu_2O NPs, the peaks at 0.97, 8.04, and 8.93 keV appeared in EDX spectrum confirming the presence of copper in the composition of Cu_2O NPs/zeolite with the copper content of about 9% (w/w). In addition, the copper content analyzed by ICP-AES was found to be of ~10.5%. Demirci et al. also reported that the copper content exchanged in zeolite A was of about 10–14% (w/w) [22]. In the studies of Razavi and Loghman-Estarki [12] and Ramya and Kanimozhi [23], the EDX spectrum was also used to confirm the presence of copper in zeolite. According to Razavi and Loghman-Estarki the copper content in the zeolite is only determined in step 1 (ion-exchange step) [12]. Thus, the second step (reduction of Cu^{2+} by hydrazine) could not influence the total copper content in the final product (Cu_2O NPs/zeolite).

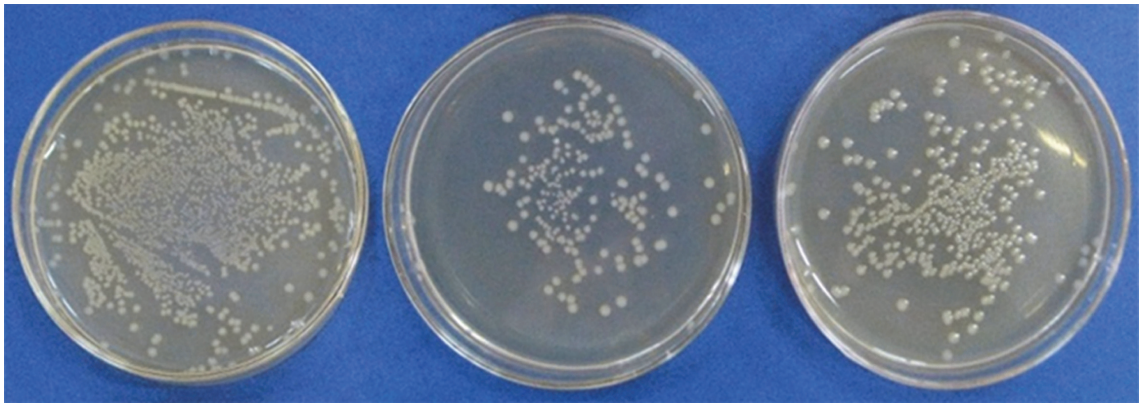
Figure 5 presented the brief schematic diagram of the synthesis procedures of Cu_2O NPs/zeolite by chemical reduction method using hydrazine hydrate.

3.2. Antibacterial Activity of Cu_2O NPs/Zeolite. The antibacterial activity of Cu^{2+}/zeolite and Cu_2O NPs/zeolite with copper concentration of 150 mg/L was presented in Figure 6 and Table 1. The obtained result indicated that the antibacterial efficiency of both Cu^{2+}/zeolite and Cu_2O NPs/zeolite against *E. coli* was of 98.15 and 96.19%, respectively.

TABLE 1: The antibacterial efficiency (η) of Cu^{2+}/zeolite and Cu_2O NPs/zeolite.

Sample	*E. coli*, CFU/mL	η, %
Control	1.13×10^8	—
Cu^{2+}/zeolite	2.09×10^7	98.15
Cu_2O NPs/zeolite	4.30×10^7	96.19

Most importantly, according to Li et al. [24], the Cu_2O NPs have low cytotoxicity. They also reported that the antibacterial efficiency of Cu_2O NPs with 4 g/L against *E. coli* and *S. aureus* could get 100% after 30 min. In our experiment with copper concentration of 500 mg/L, the antibacterial efficiency of Cu^{2+}/zeolite and Cu_2O NPs/zeolite was also attained to nearly 100% after 4 h exposure in bacterial suspension (data not shown). The antimicrobial mechanism of Cu^{2+}/zeolite can be occurred through two possible pathways as proposed by Hu et al. for Cu^{2+}/montmorillonite [25]. The first one is the adsorption of bacterial cells on the surface of the Cu^{2+} carriers and the second, Cu^{2+} ions dissociated



(a) (b) (c)

Figure 6: Photograph of the growth of *E. coli* on LB agar plates: (a) control, (b) Cu^{2+}/zeolite, and (c) Cu_2O NPs/zeolite.

from Cu^{2+}/carriers directly interact with bacterial cells. For copper-based nanoparticles (Cu, CuO, and Cu_2O nanoparticles), an elusive question remains whether the release of Cu^{2+} ions from the copper-based nanoparticles contributes to the toxicity of these nanomaterials of the toxicity exerted from the nanoparticles itself [26]. Gu et al. [27] studied the effect of Cu_2O NPs/montmorillonite on damage and removal of *M. aeruginosa* algae. The obtained results indicated that the antialgae effect mainly depended on Cu^{2+} ions extent released from Cu_2O and $^{\bullet}OH$, $O_2^{\bullet-}$ radicals generated from photocatalysis activity of Cu_2O NPs, which were responsible for the damage to cellular structure, and physiological activity led to death of algae cells.

Furthermore, the acute toxicity of $CuSO_4{\cdot}5H_2O$ for rats showed that the oral LD_{50} was 234 mg/kg body weight while oral LD_{50} of Cu^{2+}-exchanged montmorillonite with copper content of 25 g/kg was of 18 g/kg body weight [25]. This result indicated that Cu^{2+}-exchanged montmorillonite was a toxicity-free substance for rats. Thus, it can be inferred that Cu^{2+}/zeolite and also Cu_2O NPs/zeolite are less toxic than Cu^{2+} ion and both products can be used as antibacterial agent especially for water treatment and agricultural application. In some cases, where application fields require highly antibacterial activity and low cytotoxicity, Cu_2O NPs/zeolite would be more potential. In addition, Cu_2O NPs/zeolite product can be favorably produced on large scale by this process. The antifungal activity of Cu^{2+}/zeolite and Cu_2O NPs/zeolite against *Phytophthora* fungi that caused severe "foot rot" disease for pepper plant will be further evaluated for application in agriculture as the effective fungicides.

4. Conclusions

In this study, Cu_2O NPs in zeolite A were synthesized using hydrazine hydrate as a reducing agent. Structural properties of Cu_2O NPs were determined by XRD and TEM. The Cu_2O NPs have fine crystal structure with particle size of about 40 nm. Results of the antibacterial activity showed that both Cu^{2+}/zeolite and Cu_2O NPs/zeolite exhibited highly bactericidal efficiency ($\eta \sim$ 96–98%). Thus, the obtained products can be used as antimicrobial agent especially for water treatment and agricultural application.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

Nguyen Quoc Hien came up with the idea. Dang Van Phu and Le Anh Quoc designed and set up the experimental procedure. Dang Van Phu and Bui Duy Du planed the experiments and agreed with the paper's publication. Le Anh Quoc conducted the sizes measurement of as-prepared Cu_2O nanoparticles by EDX, TEM, and XRD. Nguyen Quoc Hien and Le Anh Quoc evaluated the antibacterial efficiency of as-synthesized copper products. Nguyen Quoc Hien, Bui Duy Du, and Dang Van Phu analyzed the data, drafted the manuscript, and revised the manuscript critically. All authors read and approved the final manuscript.

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