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Large-scale fabrication of colloidal nano-sized CuCl solution with high concentration for using as fungicide for plant

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Abstract

Synthesis of nano-sized CuCl with Cu concentration from 4,000 to 6,000 ppm dispersed in chitosan solution (nano-sized CuCl/CTS) using $CuSO_4.5H_2O$ as the precursor and $NaHSO_3$ as the reducing agent in HCl acid medium on large scale of 1.000 kg/batch was carried out. The obtained nano-sized CuCl/CTS samples were characterized by transmission electron microscopy (TEM) and X-ray powder diffraction (XRD). Based on the obtained results, the reaction factors for fabrication of the colloidal nano-sized CuCl/CTS solution with Cu concentration of 5,000 ppm and CuCl nanoparticle size of about 7.7 nm dispersed in 1 % chitosan solution were selected for application in agriculture as a fungicide for plant protection.

Keywords. Nano-sized CuCl, $NaHSO_3$, HCl, chitosan.

1. INTRODUCTION

Copper salts (Cu^{2+} and Cu^{+} ions) were used as fungicide for a long time due to their highly antifungal effectiveness for plants, low cost, low toxicity and after killing fungi, they turn into microelement nutrition for plants as well [1]. However, some disadvantages of using copper salts including CuCl as fungicide are of high concentration to achieve required fungicidal effect and difficul to mix with other kinds of acidic or basic fungicides. Compared to bulk CuCl, nano-sized CuCl is less toxic and possesses larger contact surface area. Furthermore, nano-sized CuCl is fairly flexible and manifests strong catalytic activity in organic reactions of linking with functional groups of enzymes especially –SH group for deactivation of fungal pathogens [1]. Therefore, for nano-sized CuCl, the required antifungal effectiveness can be achieved with lower concentration than that of the bulk CuCl. Besides, nano-sized CuCl is less sensitive to oxidation compared to the cases of nano-sized Cu and Cu_2O [1]. These later nanomaterials are easily oxidized by air oxygen, and this may cause the deterioration of their chemical properties and consequently decrease the antimicrobial activity during preservation and storage.

Metallic copper as well as cupric oxide (CuO), cuprous oxide (Cu_2O) or cuprous chloride (CuCl) nanoparticles, named as copper-based nanoparticles (Cu-based NPs) are commonly synthesized by using different copper salts as precursor such as $CuCl_2$ [2, 3], $CuSO_4$ [4], $Cu(NO_3)_2$ [5], $Cu(CH_3COO)_2$ [6] and different reducing agents such as acid ascorbic [5, 6], hydrazine [2, 7], potassium borohydride [8], sodium hypophosphite [9] together with solvent systems of polyvinyl alcohol (PVA) [2], polyethylene glycol [4], glycerin [7, 8], etc. Studies on the preparation of nano-sized CuCl have been already reported by several authors [3, 10-12]. In Vietnam, to the best of our knowledge, there has been no research on the synthesis of nano-sized CuCl reported so far.

In the present research, the fabrication of nano-sized CuCl with high Cu concentration of 4,000-6,000 ppm on large scale of 1,000 kg/batch was presented. Starting chemicals, namely $CuSO_4.5H_2O$ as precursor, $NaHSO_3$ as reducing agent, HCl and chitosan (CTS) were used for the synthesis of nano-sized CuCl. In addition, nano-sized CuCl stabilized by CTS (nano-sized CuCl/CTS) will have combined effect for enhancement of antifungal activity due to CTS also exhibiting a fungicidal effect as well [13, 14].

The reducing reaction of $CuSO_4$ to CuCl in HCl is described by the following equation (1) [15]:

$$2CuSO_4 + NaHSO_3 + 3HCl + H_2O \rightarrow 2CuCl\downarrow + NaCl + 3H_2SO_4 \quad (1)$$

2. MATERIALS AND METHODS

2.1. Materials

$CuSO_4.5H_2O$ and HCl (32 %) are industrial grade chemicals produced in Vietnam. $NaHSO_3$ (90 %), CH_3COOH (99 %) are of food grade chemicals from China. Chitosan with degree of deacetylation of ~85 %, moisture of ~10 % and average molecular weight, Mw ~10.000 g/mol was prepared at the Institute of Applied Material Science. Deionized water was used in all experiments.

2.2. Methods

2.2.1. Fabrication of nano-sized CuCl/CTS

Nano-sized CuCl materials were produced by chemical reduction method as follows:

- Preparation of CTS 10 % (w/w) solution: 55 kg CTS was soaked in 394.5 kg H_2O for 24h in a plastic tank. Then, 50.5 kg CH_3COOH was added and continuously stirred for 3 h at 300 rpm for the complete dissolving of CTS.

- Preparation of $NaHSO_3$ 3 % (w/w) solution: 33.4 kg $NaHSO_3$ (90 %) was dissolved in 966.6 kg H_2O by stirring of 30 min.

- Preparation of $CuSO_4$/CTS/HCl mixture solution: To dissolve $CuSO_4.5H_2O$ in H_2O was carried out in another plastic tank of a volume of 1,500 liters with stirring at 120 rpm. The required $CuSO_4$ concentrations were calculated as in table 1 in order to obtain nano-sized CuCl solution with Cu concentration of 4,000; 5,000 and 6,000 ppm. HCl and CTS solutions were finally added to prepare $CuSO_4$/CTS/HCl mixture solution.

- Synthesis of nano-sized CuCl: Solution of 3 % $NaHSO_3$ reducing agent was gradually added into the tank containing $CuSO_4$/CTS/HCl mixture solution. The reaction mixture was stirred for about 4h for Cu^{2+} reducing to Cu^{+} completely and formed as nano-sized CuCl with white color.

Table 1: Formulation of chemicals for fabrication of colloidal nano-sized CuCl solution with different Cu and CTS concentration on the scale of 1,000 kg/batch

No.	$CuSO_4.5H_2O/H_2O$ (kg/kg)	$NaHSO_3$ 3 % solution (kg)	HCl 32 % (kg)	CTS 10 % solution (kg)	Cu concentration (ppm)
1	15.6/677.4	200	7	100	4,000
2	19.5/571.5	300	9	100	5,000
3	23.4/465.6	400	11	100	6,000
4	19.5/521.5	300	9	150	5,000
5	19.5/621.5	300	9	50	5,000

2.2.2. Characterization of nano-sized CuCl

Nano-sized CuCl/CTS products were characterized by X-ray diffraction (XRD) on D8 Avance Bruker, Germany with 2θ in the range from 5 to 70^o [3, 11]. The CuCl nanoparticle sizes were evaluated using a transmission electron microscope (TEM), JEM 1010, JEOL, Tokyo, Japan [3, 10, 11]. Nano-sized CuCl/CTS powder used for XRD characterization was obtained by coagulation of nano-sized CuCl/CTS solution with C_2H_5OH. CuCl particle size was statistically calculated by Photoshop CS6 and Microsoft EXCEL 2010 softwares.

3. RESULTS AND DISCUSSION

3.1. Dependence of CuCl nanoparticle size on initial Cu^{2+} concentration

The average particle size of nano-sized CuCl dispersed in 1 % CTS was of 5.5, 7.7 and 11.8 nm for Cu^{2+} concentration of 4,000; 5,000 and 6,000 ppm, respectively calculated from TEM images of nano-sized CuCl in Figure 1 (A,B,C). The obtained results indicated that the higher the Cu^{2+} ions the larger the CuCl nanoparticle size is. Results of our previous study also confirmed that the higher the initial metal ions precursor concentration (Ag^{+}), the larger the metal nanoparticles size (Ag nano) [16]. In addition, TEM images in Figure 1 also indicated that the morphology of nano-sized CuCl was quasi-spherical and the particle size distribution was of the Gaussian mode (bell-shaped distribution) with fairly narrow distribution scope. The obtained results also proved CTS as an effective stabilizer to protect nano-sized CuCl from agglomeration to form larger particle size.

The nano-sized CuCl/CTS products with Cu concentration of 5,000-6,000 ppm are useful for utilization as fungicide for plants due to the comfortable market demand commonly for dilution of 1 liter to 250 liters applied for 1 ha of plant and nano-sized CuCl/CTS with Cu concentration of about 20-30 ppm is attained effective activity to exterminate fungal pathogens as a result obtained in our previous research [17]. Therefore, the nano-sized CuCl/CTS product with Cu concentration of 5,000 ppm was selected to use as fungicide for plants due to this product has smaller particle size (7.7 nm) compared with that (11.8 nm) of 6,000 ppm. It was generally accepted that the smaller the particle size the higher the antimicrobial activity [18].

3.2. Dependence of CuCl nanoparticle size on CTS concentration

Cu^{2+} ions –CTS complex was formed owing to CTS having –OH and $–NH_2$ functional groups [19]. The synthetic process of nano-sized CuCl stabilized by CTS is described in figure 2.

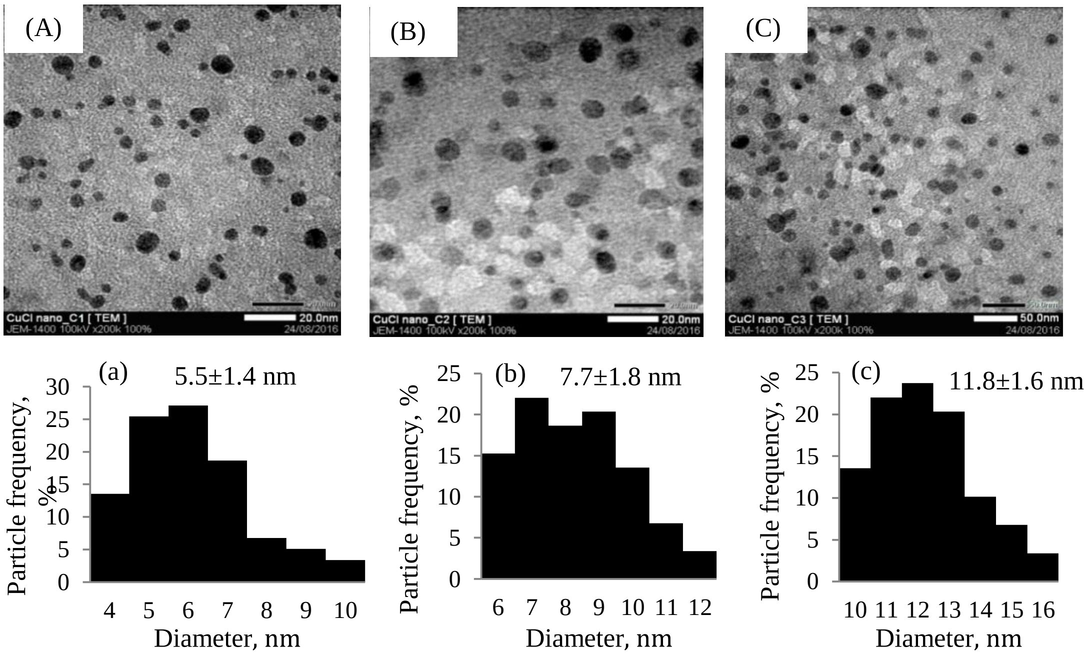

Figure 1: TEM images (A,B,C) and particle size distribution (a,b,c) of nano-sized CuCl: 4,000 ppm (A,a), 5,000 ppm (B,b) and 6,000 ppm (C,c)

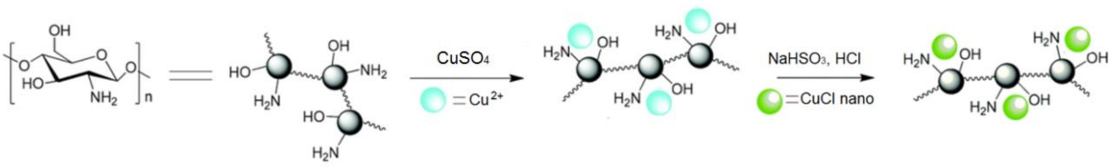

Figure 2: Shematic illustration of the synthetic process of nano-sized CuCl stabilized by CTS

Cu^{2+} ions were reduced to Cu^{+} (CuCl) by $NaHSO_3$ in HCl as presented in Eq. 1 [15]. The resulted CuCl molecules aggregate to CuCl clusters and these CuCl clusters agglomerate with other nearby to create CuCl nanoparticles under the protection of CTS from aggregation of CuCl clusters to form large CuCl particles. From TEM images in figure 3 (A,B,C), the average size of CuCl nanoparticles was calculated to be of 16.4, 7.7 and 8.1 nm for CTS concentration of 0.5, 1.0 and 1.5 %, respectively. Accordingly, the size of CuCl nanoparticles stabilized by CTS decreased with the increase of CTS concentration. It was already reported that the higher the stabilizer concentration (PVA), the smaller the nanoparticle size (Ag nano) [20]. In case of Ag nano (20 mM), PVA concentration of 2-3 % was found out as a critical range to obtain the smallest Ag nanoparticle size (10 nm). In the case of nano-sized CuCl with Cu concentration of 5,000 ppm, the critical concentration of chitosan stabilizer was specified to be of 1.0-1.5 % to create the smallest nano-sized

CuCl (7.7-8.1 nm).

Therefore, the CTS concentration of 1 % was selected for the fabrication of nano-sized CuCl with Cu concentration of 5,000 ppm for utilization as fungicide to protect plants.

3.3. X-ray diffraction characterization

The XRD pattern of nano-sized CuCl/CTS in figure 4a exhibited 4 characteristic peaks particularly at 2θ ~28.5^o; 33.1^o; 47.4^o and 56.3^o that corresponding to (111), (200), (220) and (311) planes of CuCl crystalline structure [10, 11]. The peak positions were in good agreement with those for CuCl standard pattern obtained from the International Center of Diffraction Data card (ICDD, formerly JCPDS, card no. 06-0344) (figure 4b) [10]. In addition, the XRD pattern in Figure 4a also showed two characteristic peaks for CTS at 2θ ~10.1^o and 20.3^o that were the same as the XRD pattern of CTS in figure 4c [21].

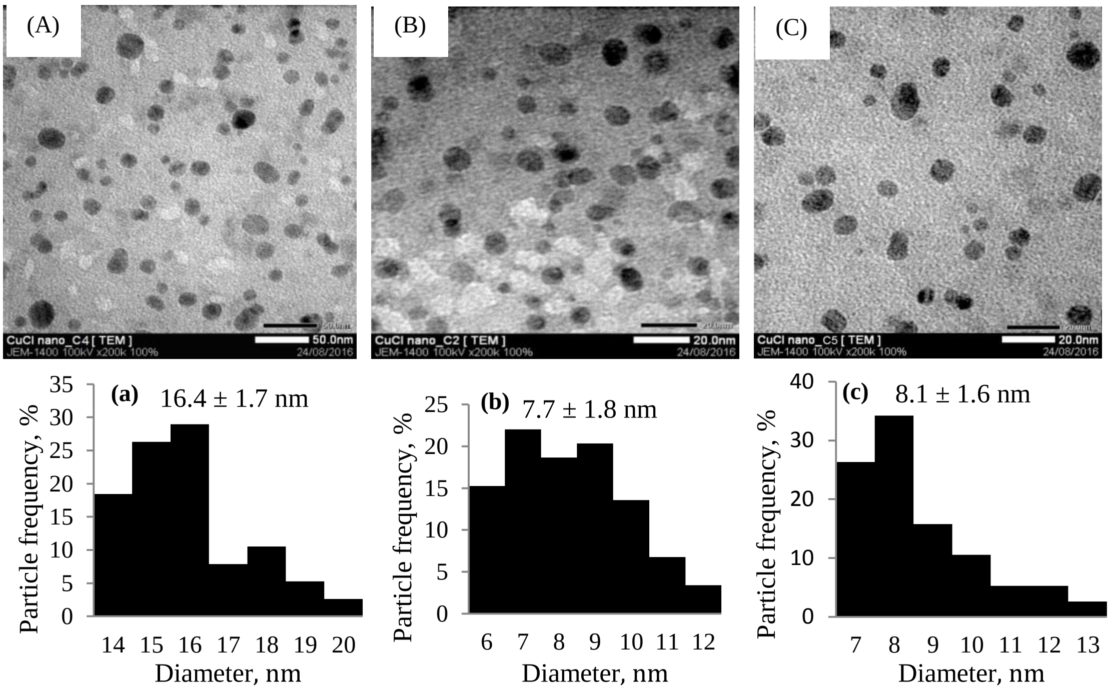

Figure 3: TEM images (A,B,C) and particle size distribution (a,b,c) of nano-sized CuCl with different CTS concentration: 0.5 % (A,a), 1 % (B, b) and 1.5 % (C,c)

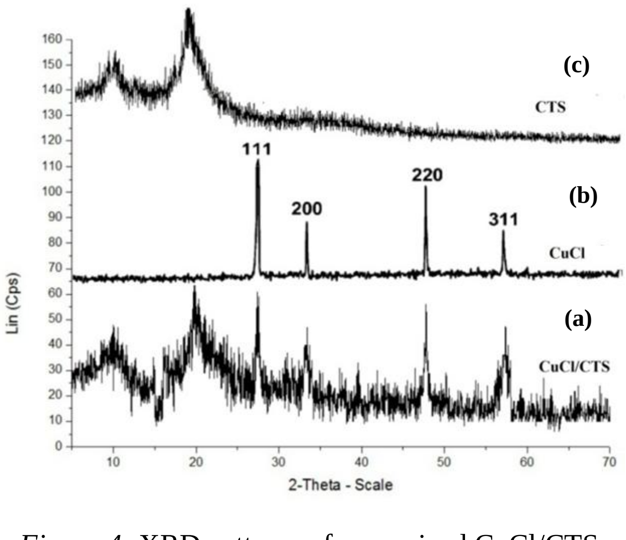

Figure 4: XRD patterns of nano-sized CuCl/CTS (a), reference CuCl (b) and CTS (c)

4. CONCLUSION

The study on the synthesis of colloidal nano-sized CuCl/CTS solution with high Cu concentration (4,000-6,000 ppm) on large scale of 1,000 kg/batch was carried out. The particle size of nano-sized CuCl depended on the initial Cu^{2+} ions precursor and CTS stabilizer concentrations. The chemical formulation and the reaction factors for fabrication of the colloidal nano-sized CuCl/CTS solution with Cu concentration of 5,000 ppm and CuCl nanoparticle size of about 7.7 nm were selected as the concentration of reducing agent $NaHSO_3$ of 0.9 %, the CTS stabilizer concentration of 1 %, stirring speed of 120 rpm and the reducing reaction time of 4h. The resulted nano-sized CuCl/CTS with 5,000 ppm Cu concentration is considered as a suitable product for utilization in agriculture production as a fungicide for plant protection.

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