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GREEN SYNTHESIS OF COPPER NANOPARTICLES COLLOIDAL SOLUTIONS AND USED AS PINK DISEASE TREATMENT DRUG FOR RUBBER TREE

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ABSTRACT

Copper oxalate complex were prepared by Copper (II) sulfate and oxalic acide and were identified by XRD. This complex were used as a precusor to prepare colloidal solutions of metallic copper nanoparticles in Microwave condition with protectant agent such as PVP 55,000, PVP 1,000,000 and glycerine media. Copper nanoparticles colloidal solutions were characterized by X-ray diffraction, UV-Vis, TEM. XRD analysis revealed broad pattern for fcc crystal structure of copper metal. UV-Vis showed an absorption of copper nanoparticles at 595-600nm. TEM analysis demontrated copper nanoparticles with an average diameter of about 6nm. This colloidal solution was used as anti Pink Disease drug for rubber tree at low concentration (dose of resistance fungus of about 5-7ppm and dose of kill fungus of about 10ppm).
Keyword: Corticium Salmonocolor, Pink Disease, copper nanoparticles, rubber tree

INTRODUCTION

Among various metal particles, copper nanoparticles have attracted considerable attention because copper is one of the most important metals in modern technology [1]. Considerable interest has been focused on copper nanoparticles due to their optical, catalytic, mechanical and electrical properties [2]. The advantages of Cu nanoparticles are cheap, high yields in mild reaction conditions and have short reaction times compared to traditional catalysts [3]. Cu nanoparticles have been synthesized through different methods such as thermal decomposition [2], metal salt reduction [3] microwave heating [6], radiation methods [6], micro emulsion techniques [6], …..

Pink Disease (Scientific Name: Macrophoma mangiferae) is caused by fungus of *Corticium Salmonocolor*. This disease was named after the light pink color of the rubber tree branches that was infected by it with 1 of the bark of the branches growing with fungis like a spider web. This disease causes damage to the trunk of the rubber trees, it is dangerous and be able damages to mainly major branches of the tree; especially those from 2 to 7 years of age. This type of disease mainly occers in the rainy season and peaks at the months of July, August, with the reasonable temperature of 20-30^{0}C, and the humidity level above 80%. This type of disease are more common at places where there is little to no room for the water to escape, usually floooded areas. Pink Disease is a common disease on the trunks of wood trees in tropical areas in of the world. Areas in which the rain level is above 250 mm/month along with hot and humid days in the rainy season, are the perfect place for this kind of disease to grow.

Recently, our group reported the synthesis of uniformsized nanoparticles of copper nanoparticles from thermal decomposition of copper oxalate complexes [7]. In this report, colloidal solution of copper nanoparticles were going on synthesizing by polyol method from copper oxalate as a precursor. This colloidal solution was used as Pink Disease treatment drugs for rubber tree.

EXPERIMENTAL

Materials

- Copper Sulfate $CuSO_4.5H_2O$ (Merck, 99%)
- Acid oxalic (Merck, 99%)
- Milipore Water (Merck, 99%)
- Polyvinyl pyrolidone (PVP, Mw ≈ 1,000,000 BASF-Germany, 99%)
- Glycerine (99%, AR-China)

All the chemicals reagents used in our experiments were used as received without further purification.

Synthesis of copper oxalate

Copper oxalate precursor was synthesized according to this procedure: the $CuSO_4.5H_2O$ (2 mmol) was dissolved into 50 ml of DI water (Merck) to form a homogeneous solution. A stoichiometric amount of acid oxalic dissolved in an equal volume of DI water and was dropwise added into the above solution under magnetic stirring. The solution was stirred for about 15 min and a blue precipitate was centrifuged and washed by water to pH=7 and by ethanol several times. The product was dried at 50^0C. The copper oxalate, CuC_2O_4, was characterized by FE-SEM, powder X-ray diffraction (XRD).

Synthesis of Cu nanoparticles

Poly(N-vinylpyrrolidone) acting as a capping agent, was dissolved in glycerine and heated with stirring in an oil bath at temperature reaction (180-200^0C). Copper Oxalate was then added into the hot reaction medium and was heated until the color of this solution changes to cloudy orange.

Characterization

UV-Vis absortion were received by UV-Vis (NIR-V670-Jacco Japan, UNS-VNU). XRD patterns were recorded by a D8 Advance, Bruker - Germany (Institute of Applied Materials Science-VAST).Field Emission Scanning electron microscopy (FE-SEM) images were obtained on S4800 – Hitachi, SHTP Park, HCM city. Transmission electron microscopy (TEM) images were obtained on a JEM-1400, Japan ,UT-VNU.

Microbiological tests

Corticium Salmonocolor were supplied by Faculty of Biology, University of Natural Sciences, VNU-HCMC**.** Antifungal effects of the Cu colloidal solutions were studied by culture medium toxicity method in PGA media (Petri Dish).

RESULTS AND DISCUSSION

Precusor of copper oxalate

Copper oxalate was prepared with high yield and confirmed by powder XRD (Fig.1). The interplanar *d*-spacings of the corresponding lines presented in the powder XRD pattern match those of standard sample, which corresponded to the primitive monoclinic system. Moreover, it was clear from XRD that no other phases of copper oxalate was presented in the as-synthesized copper oxalate. The FE-SEM image of copper oxalate showed particles in the size range of under 150 nm (Fig. 2).

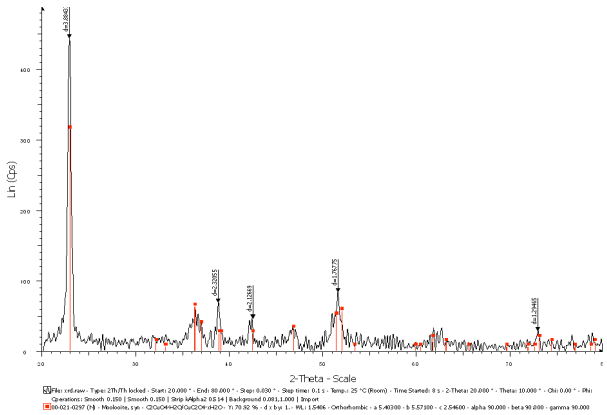

Fig. 1. *XRD pattern of copper oxalate.*

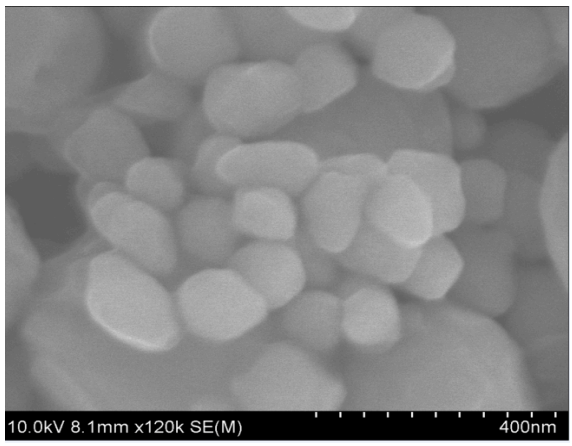

Fig. 2. *The FE-SEM image of copper oxalate*

***Synthesis of copper* colloidal solutions**

Table 1. *Copper colloidal solutions*

Sample	Glycerin (ml)	CuC_2O_4 (g)	PVP 55000 (g)	CuC_2O_4 : PVP	Temp. (^{0}C)	Wave lenghth (UV-Vis)
1	60	0,01	0,20	1 : 20	240	586
2	60	0,01	0,15	1 : 15	240	590
3	60	0,01	0,10	1 : 10	240	587
4	60	0,01	0,05	1 : 5	240	597
5	**60**	**0,01**	**0,01**	**1 : 1**	**240**	598
6	60	0,05	0,01	5 : 1	240	589
7	60	0,10	0,01	10 : 1	240	591
8	60	0,15	0,01	15 : 1	240	591
9	60	0,20	0,01	20 : 1	240	594

The results from UV-Vis of the samples was illustrated in the Fig. 3. Nanosized particles exhibit unique optical properties with an exponential-decay Mie scattering profile with decreasing photon energy. In this reports, all of experiments from 1 to 9 show an absorption peaks of copper nanoparticles at from 586 to 594nm. The synthesized copper colloidal solutions were stable for over 2 months, especially the 5th samples stable for over 3 months. The stabilization of copper colloidal solutions were due to the capping of nanoparticles by PVP 55,000 in reaction process. The 5th sample were testing to treatment Pink disease for Rubber Tree.

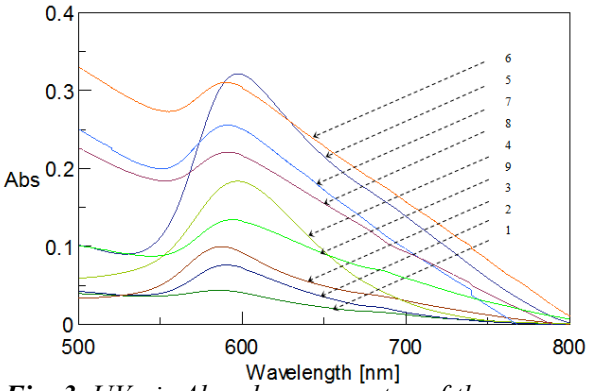

Fig. 3. *UV-vis Absorbance spectra of the copper colloidal solutions*

Characteristics of CuNPs

Copper colloidal solutions were coating on the glass of microscopy by spin coating and baked at 300^{0}C. The X-ray diffraction patterns which were corresponded to crystalline copper characteristic peaks with a face-centered-cubic (fcc) crystal structure at 2θ value of 43,60 , 50,70 and 74,50 representing (111), (200) and (220) planes of fcc structure of copper (Fig. 4).

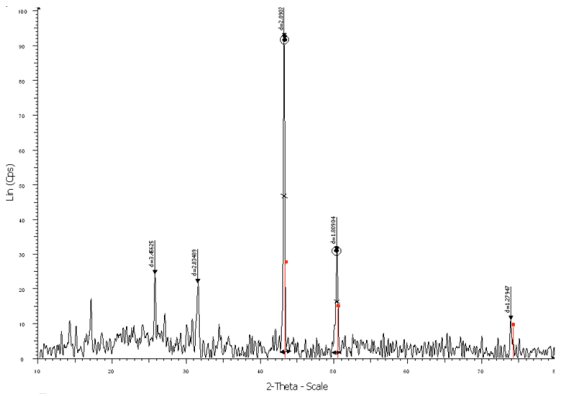

Fig. 4*. X-ray diffraction patterns of CuNPs-PVP*

Characterized by TEM

The TEM image of the 5th sample showed that the average size of copper nanoparticles was about 6nm.

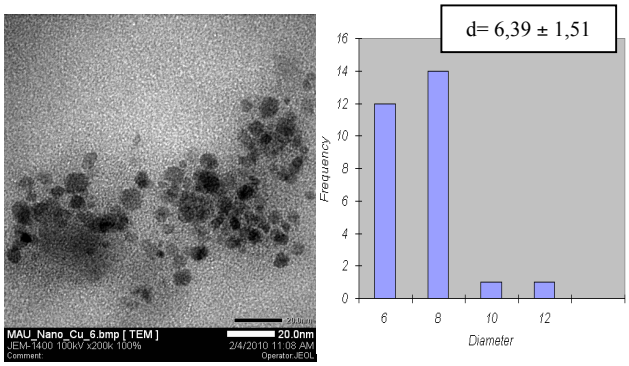

Fig. 5. *TEM image and histogram of copper nanoparticle size ditribution in 5th sample.*

Microbiological tests

Corticium Salmonocolor were supplied by Faculty of Biology, University of Natural Sciences, VNU-HCMC**.** Antifungal effects of the Cu colloidal solutions were studied by culture medium toxicity method in PAG media (Petri Dish) and spraying method. This colloidal solution was used as anti *Pink Disease* drug for rubber tree at low concentration (dose of resistance fungus of about 5-7ppm (Fig.6) and dose of kill fungus of about 10ppm (Fig.7).

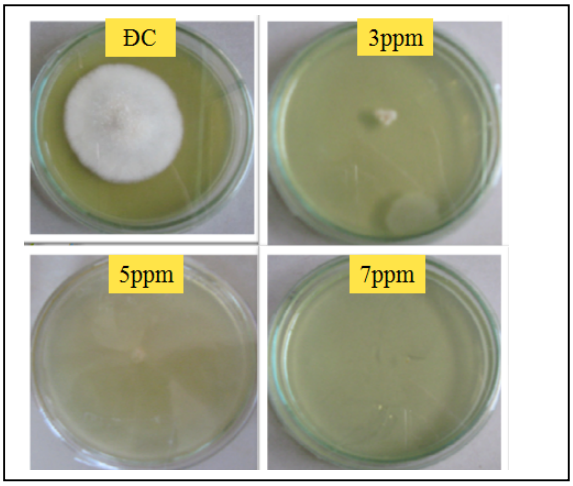

Fig. 6. Anti-Corticium Salmonicolor Testing *(Corticium Salmonicolor was found at Control Sample (ĐC) after 7 days and wasn't found at nano copper solution samples with concentration of 5-7ppm after 15 days*

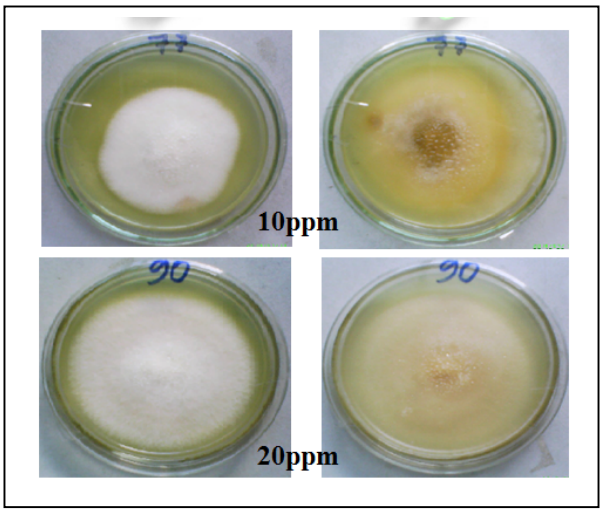

Fig. 7. Kill-Corticium Salmonicolor Testing *(Corticium Salmonicolor was found at Control Sample (ĐC) after 15 days and wasn't found at nanocopper solution samples with concentration of 10-20ppm after the first spraying (after15 days)*

CONCLUSIONS

Copper colloidial solutions had been synthesized rapidly in chemical green condition, without reagent. The UV-Vis spectra showed that these as-synthesis samples had absorbance peak from 588 to 598nm. The average size of copper nanoparticles was about 6nm via TEM images.

This colloidal solution was used as anti *Pink Disease* drug for rubber tree at low concentration (dose of resistance fungus of about 5-7ppm and dose of kill fungus of about 10ppm).

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