Innovative environmentally friendly technology for copper(II) hydroxide production

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Abstract

The innovative laboratory procedure for the synthesis of copper(II) hydroxide in the form of the aqueous suspension was developed. The reaction mechanism consists of the reaction between copper(II) sulphate pentahydrate and sodium carbonate by successive ion exchange of carbonate ions with the hydroxide ones in a multistep process. Production of copper(II) carbonate and sodium sulphate by reacting of copper(II) sulphate with sodium carbonate was followed by addition of sodium hydroxide solution whereby the product, copper(II) hydroxide, was obtained by releasing an equimolar amount of sodium carbonate. It was determined that, the equimolar reaction of copper(II) sulphate and sodium hydroxide lead to the maximal reactants exploitation. Sodium phosphate, formed in the final process stage by addition of 10 % phosphoric acid solution, acted as a copper(II) hydroxide stabilizer. High yield of the product was obtained by optimizing the synthesis parameters: reaction time, molar ratio of reactants and the reaction temperature. The obtained product was formulated to obtain a commercial product, which is used as a fungicide and bactericide.

Keywords: *copper(II) hydroxide; fungicide; plant protection; synthesis*

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1. INTRODUCTION

A sustainable approach to the protection of plants and control of the plant harmful organisms is the application of agro-technical, physical, biological and chemical measures in a way that minimizes economic, health and environmental risks [1]. This is a set of good agricultural practices necessary for the production of useful and profitable products. Plant protection does not imply the complete exclusion of pesticides, but their rational use, which should result in increased yields and profitability of production, and also environmentally friendly production methods [2]. Copper-based preparations have been widely used in this approach. Fungicides, used to control the causative agents of diseases in plantations of fruit trees, vines and ornamental grass, can be applied throughout the year. The main advantage of copper-based preparations is that copper usually remains attached to the surface layer of the soil and does not contribute to phytotoxicity [3]. Copper persistence is conditioned by strong bonding to organic matter, mineral clays and oxides of iron, aluminum and manganese [4]. More recently, research tendencies have been focused on the development of technologies and environmentally friendly preparations [5], while some of them bring to product/plant deficiency such as degradation [6]. It was also shown that copper-based preparations are effective against parasites [7].

Most of the known industrial processes for copper(II) hydroxide production start from the metallic copper, which is dissolved and oxidized using nitric acid to obtain Cu^{2+} ions with evolution of NO_2 gas, as shown in the equation (1). Further, addition of hydroxide ions displaces water from the copper(II) ion surrounding shell, yielding copper(II) hydroxide, $Cu(OH)_2$, as a light blue precipitate, equation (2).

$$Cu_{(s)} + 4H_3O^+_{(aq)} + 2NO^-_{3(aq)} = (Cu(H_2O)_6)^{2+}_{(aq)} + 2NO_{2(g)} \qquad (1)$$

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$$(Cu(H_2O)_6)^{2+}_{(aq)} + OH^- = Cu(OH)_{2(s)} + 6H_2O_{(l)} \quad (2)$$

At the industrial level, during the 17th and 18th century, copper(II) hydroxide was produced and used in pigments, such as verditer blue and Bremen green, as well as in production of ceramics and painting [8,9]. In a solution of ammonia, known as Schweizer's reagent, it can dissolve cellulose and it is therefore used in the production of rayon and cellulose fibers. It is also used in the aquarium industry for protecting fish from parasites, as an alternative to the Bordeaux mixture, fungicides and nematicides [10,11].

Copper(II) hydroxide is the best copper form to control these diseases, and the highest content of this compound is found in some commercial preparations such as Funguran-OH, Blauvit, Erevest, Cuprozin 35 WP, Champion WG 50, Cuproline, Kocide DF, Fungohem-SC, Blue Jet 50-DF *etc*. The fungicidal activity of copper-based compounds prevents formation/reproduction of pathogens exhibiting besides the fungicidal, also the bactericidal activity [19].

The main advantage of copper(II) hydroxide with respect to other copper-based formulations (*e.*g. Bordeaux mixture containing $Cu(OH)_2$ and $CuSO_4$, copper based fungicides in the form of $CuCl_2·3Cu(OH)_2$ and mixtures of CuO and $Cu(OH)_2$ is in the formation of a stable solid copper form with slow/controlled releasing behavior which exerts more effective impacts on the disease.

The available scientific and professional literature indicates an insufficient number of reports on the laboratory synthesis of this compound. Although effective methods for the preparation of $Cu(OH)_2$ are available, there is still a necessity for evaluation of its storage and thermal stability, kinetic release behavior, activity, environmental impact etc. Under certain conditions (temperature, pH), $Cu(OH)_2$ is thermodynamically unstable and gradually or rapidly undergoes to a more stable CuO form [20, 21]. The degradation of copper(II) hydroxide to CuO can be monitored by a number of methods, including X-ray diffraction and colorimetric methods. Knowledge about product stability, *i.e.* decomposition rate during storage, is an important parameter that is used for development of appropriate techniques for stabilization such as using aqueous solutions of phosphate and their salts [22].

Coper(II) hydroxide can be produced by adding sodium hydroxide (NaOH) to a dilute solution of copper(II) sulphate ($CuSO_4·5H_2O$) [16]. However, in this process, it often captures water in the crystal lattice, as well as impurities and NaOH. If ammonium chloride (NH_4Cl) is added to the mentioned solution, a slightly cleaner product can be obtained [21]. An easy method to obtain $Cu(OH)_2$ is by electrolysis of water, which contains electrolytes such as sodium sulphate (Na_2SO_4) or magnesium sulphate ($MgSO_4$), whereby old copper is used as the copper anode [23]. Synthesis of $Cu(OH)_2$ can be also carried out starting from the $Na_2Cu(OH)_4$ salt in a solid state. In order to prevent the formation of CuO from the $Cu(OH)_4^{2-}$ complex during the synthesis process, the solution is diluted with a large amount of water. By this procedure, a solid crystalline product which crystallized relatively well, resulted in a valuable product [24]. Many of synthetic derivatives of $Cu(OH)_2$ have also been studied [25]. Copper(II) hydroxide can be used in a mixture with other biologically active compounds or agents for the formation of multi-component pesticides and fungicides, providing a wide range of agricultural protection [26]. Although many products are commercially available for these purposes, there is still a need for new ones that are more efficient, cheaper, less toxic and environmentally safe or have different modes of operation.

This paper describes a new environmentally friendly process for the synthesis of $Cu(OH)_2$, which is used as a fungicide and bactericide. This process consists of the reaction of copper(II) sulphate pentahydrate and sodium carbonate in the first step, followed by multistep process of carbonate ion exchange with hydroxide ion until an aqueous suspension of desired product is obtained. Reaction parameters such as reaction time, molar ratio of reactants and reaction temperature were varied in order to define an optimal laboratory procedure that was successfully scaled-up at industrial level.

2.EXPERIMENTAL PART

2. 1. Materials

Sodium carbonate (*p.a.*, ACS reagent, 99.9 %), copper(II) sulphate pentahydrate (ACS reagent, ≥98.0 %), sodium hydroxide (ACS reagent, ≥97.0 %), and concentrated phosphoric acid (*p.a.* 75 %), Tensiofix LX Special (S.A. Ajinomoto OmniChem N.V., Belgium, ≥95.0 %), Supragil WP (Solvay, Belgium, ≥95.0 %) and kaoline (KaOLIN a.d. Valjevo) were kindly provided by the company H.I. Župa Kruševac (Serbia). All chemicals were used as received without further purification.

2. 2. Synthesis of copper(II) hydroxide by an optimized laboratory procedure

In the experimental work, the process of synthesis of copper(II) hydroxide was optimized with respect to synthesis parameters: reaction time (2-2.5 hours), molar ratio of reactants ($CuSO_4·5H_2O:NaOH:Na_2CO_3$=0.523-0.575:1.045--1.150:0.066-0.072) and reaction temperature (25-30 °C). Adjustment of the percentage of suspension in the product obtained to be in the range 5.0-6.0 % was performed as well. The production of the copper(II) hydroxide was carried out in four phases: the synthesis reaction of copper(II) hydroxide suspension, filtration and washing, drying, and grinding with introduction of additives to formulate the final commercial product.

General procedure for copper(II) hydroxide synthesis is as follow: in a three-necked round flask of 250 cm^3 equipped with a magnetic stirrer, condenser, thermometer and a dropping funnel, 7.0 g of 98 % (0.066 mol) sodium carbonate was dissolved in 74.0 cm^3 of water. Next, a 22 mass.% solution of copper(II) sulphate was prepared by dissolving 130.7 g of 98 % (0.523 mol) of copper(II) sulphate pentahydrate in 403.3 cm^3 of water, and a 14 % sodium hydroxide solution was obtained by dissolving 41.8 g of 98 % (1.046 mol) of sodium hydroxide in 251.1 cm^3 of water. After dissolution of sodium carbonate, 1/10 of the volume of the prepared copper(II) sulphate solution was added slowly, using a dropping funnel, for 10 minutes under mixing. The pH value of the reaction mixture, at this point was between 7.5 and 8. Hereafter, 1/10 of the volume of the 14 % solution of sodium hydroxide was added at once from a dropping funnel, and stirring was continued for 2 minutes. The pH of the reaction mixture was 13. Successive additions of 1/10 of the volume of the copper(II) sulphate solution for 10 minutes with mixing for 10 minutes, and then 1/10 of the volume of the 14 % sodium hydroxide solution followed by mixing for 2 minutes was performed until reactants were spent. In the course of reaction, the temperature was maintained at 30 ^oC and pH in the range from 7.5 to 8.5 using the NaOH solution or phosphoric acid. After that, the prepared phosphoric acid solution (12 cm^3 of 75 % H_3PO_4 and 88 cm^3 of water) was added and the reaction mixture was further stirred for another 5 minutes. When the reaction was complete the pH value was found to be in the range from 7.5 to 8.5. The reaction mixture was filtered using a Buhner's funnel, and the solids were washed with water to reach a negative reaction to the sulphate ion and then dried at the temperature of 65 ^oC to the moisture content below 1 %. The obtained product, copper(II) hydroxide, was analyzed for contents of copper, sulphate, carbonate, phosphate as well as the pH value.

2. 3. Synthesis of copper(II) hydroxide at the industrial level

The production of copper(II) hydroxide was performed in four phases. The first phase was the synthesis of copper(II) hydroxide in the reactor, followed by filtration of the obtained suspension, then drying of the filter cake and finally the fourth stage was simultaneous grinding and formulation of the final product. After the grinding phase and formulation, the product was packed in a designed packaging bag.

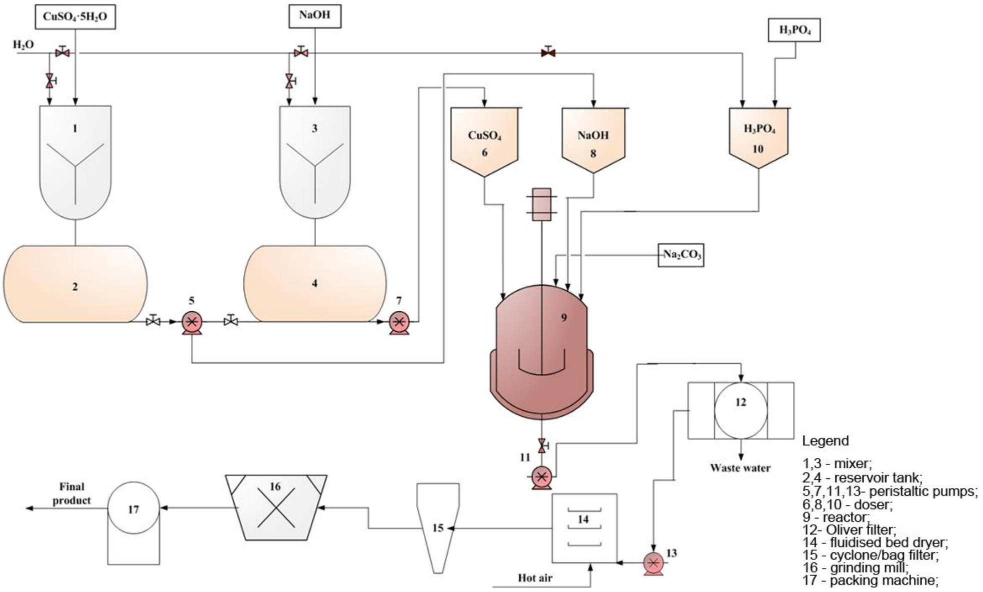

Figure 1. Schematic overview of the technological process for the production of copper(II) hydroxide

Figure 1 presents the scheme of the industrial process for the production of copper(II) hydroxide and formulation to the commercial product BLAUVIT (H.I. Župa Kruševac, Serbia). First, a 22 % solution of copper(II) sulphate was prepared in the mixer 1, and a 14 % sodium hydroxide solution was prepared in the mixer 3, (Fig. 1). Sodium hydroxide and copper(II) sulphate solutions were prepared for multiple production batches and were collected in reservoir tanks 2 and 4. Using the pumps 5 and 7, the solutions were transferred to the dozers 6 and 8. In the reactor, sodium carbonate was dissolved in the required amount of water, after which, the 1/10 of the total amount of copper(II) sulphate solution from the dozer was added to the reactor 9 in the controlled manner for 10 minutes. Then, the required amount (1/10 of the total amount) of sodium hydroxide solution – (position 8, Fig 1.) was added at once and the reaction mixture was mixing for two minutes. Successive addition of copper(II) sulphate and sodium hydroxide was continued until the total of ten batches of reactants were added, and followed by neutralization with addition of required amount of phosphoric acid solution from the dozer 10. Mixing was continued while controlling the pH between 7.5 and 8.5 using the NaOH solution or phosphoric acid.

After completion of the reaction, the reaction mixture was transferred using a pump 11, to the filtration device, *i.e.* continuous operation filter (Oliver filter) (position 12, Fig. 1). The obtained wet filter cake was transferred by a peristaltic pump 13, to a fluidized bed dryer 14. The particles from the dryer were collected in a cyclone and a bag filter (position 15, Fig. 1) into the collecting bags and were transported to the grinding and formulating mill 16, where the required quantities of fillers/additives were introduced and compounded to obtain the homogeneous product. The formulated BLAUVIT preparation was packed using a packing machine 17, (Fig. 1) and stored in the final product warehouse.

2. 4. Characterization methods

Analysis of the obtained product was carried out by known analytical methods for the contents of copper, sulphate, carbonate, phosphate as well as the pH value.

Fourier transforms infrared spectroscopy (FTIR) spectra of the samples were recorded in absorbance mode using a Nicolet™ iS™ 10 FT-IR Spectrometer (Thermo Fisher SCIENTIFIC, USA) spectrometer with Smart iTR™ Attenuated Total Reflectance (ATR) Sampling accessories, within a range of 400-4000 cm^{-1}, at a resolution of 4 cm^{-1} and in 20 scan mode.

A laboratory pH meter, Mettler Toledo FE20/FG2 (Switzerland), with the accuracy of ±0.01 pH units, was used for pH measurements.

The copper content was determined according to Standard Method for the Examination of Water and Waste water [27], using an Atomic Absorption Spectrophotometer (Spectra AA 55 Varian - Flame mercury system FIAS-oven, USA).

The content of sulphate was determined according to a method described in literature. This method involves measurements of the turbidity formed (barium sulphate) when an aliquot of barium-chloride-gelatine reagent is added to an acidified sample [28].

Phosphate was determined by a colorimetric method using an UV-Vis spectrophotometer (Shimadzu 1700 UV/Vis spectrophotometer, Japan).

The carbonate content was determined by a standard titration method, where calcium and magnesium ions in the sample were sequestered upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction was detected by means of Eriochrome Black T indicator, which is red colored in the presence of calcium and magnesium and blue colored when the cations are sequestered [29,30].

3. RESULTS AND DISCUSSION

In this paper, an optimal laboratory procedure for the synthesis of copper(II) hydroxide was defined. In laboratory experiments, the reaction parameters such as reaction time, molar ratio of reactants and reaction temperature were defined. Also, based on the obtained laboratory results, the technology transfer to industrial synthesis was conducted in the company H.I. Župa Kruševac (Serbia).

The synthesis reaction was performed by the following mechanism: in the first step copper(II) sulphate reacted with sodium carbonate, according to the reaction:

$$CuSO_{4(aq)} + Na_2CO_{3(aq)} = CuCO_{3(aq)} + Na_2SO_{4(aq)} \quad (3)$$

In the second step sodium hydroxide reacted with the resulting copper(II) carbonate to produce copper(II) hydroxide by generating an equimolar amount of sodium carbonate:

$$CuCO_{3(aq)} + 2NaOH_{(aq)} = Cu(OH)_{2(s)} + Na_2CO_{3(aq)} \quad (4)$$

Generated sodium carbonate reacted with a new portion of copper(II) sulphate producing copper(II) carbonates, and thus the reaction proceeded successively. Due to low solubility of the copper(II) hydroxide in water, at the end of reaction an aqueous suspension was obtained, and further processed by filtration, washing with plenty of water, dried and milled to a particle diameter below 70 microns. Concomitantly, in the course of milling, appropriate filler/additives (Tenziofix LX, Supragil WP and kaoline) were introduced to obtain commercial product - BLAUVIT.

The obtained results, related to optimization of the synthesis procedure of copper(II) hydroxide at the laboratory level, are shown in Table 1.

Based on the results presented in Table 1, it can be seen that the highest yields of 93.5 % and 93.2 % were obtained in the experiments **6** and **1**, respectively. In the experiment **1**, the molar ratio of reactants: $CuSO_4 \cdot 5H_2O$: NaOH: Na_2CO_3 was 1.0:2.0:0.125, while in the experiment **6** the excess of 10 % Na_2CO_3 solution was used. In the experiment **4**, excess of the copper(II) sulphate pentahydrate was used, and in the experiment **5** sodium hydroxide was added in excess. In both cases, lower yields were achieved, as compared to experiments **1** and **6**, due to the changes in reactant molar ratios. Using of copper(II) sulphate at a non-stoichiometric ratio results in the unfavorable effect on the product yield. Excess of sodium hydroxide negatively influences the formation of the product due to subsequent transformation of the produced copper(II) hydroxide to copper(II) oxide, as shown by the equation (5). Higher amounts of sodium hydroxide contribute to a lower quality product, which has to be subsequently processed/purified to obtain quality according to customer/market demands. An alternative for solving the unfavorable effect of increased pH was achieved in two ways: i) sodium hydroxide addition to the reaction mixture was followed by immediate addition of copper(II) sulphate or ii) by controlled addition of both reactants by using flowmeters (or by using pH stat equipment). Black colored copper(II) oxide, as by-product, could be also formed if the reaction takes place at higher temperature, *e.g*. in experiment 2 (Table 1):

$$Cu(OH)_{2(s)} = CuO_{(s)} + H_2O_{(l)} \qquad (5)$$

Table 1. Results of copper(II) hydroxide synthesis under different reaction conditions

Exp.	Molar ratio of reactants			Reaction temperature, °C	Reaction time, h	Suspension, %	pH	Yield, g	Yield, %
	$CuSO_4 \cdot 5H_2O$	NaOH	Na_2CO_3						
1	0.523	1.046	0.066	30.0	2.0	5.3	8.0	47.50	93.2
2	0.523	1.046	0.066	45.0	2.5	6.0	7.8	40.80	80.0
3	0.523	1.046	0.066	25.0	2.0	5.5	7.8	47.16	92.5
4	0.575	1.046	0.066	28.0	2.0	5.5	7.4	44.36	87.0
5	0.523	1.150	0.066	28.0	2.0	5.5	8.2	43.85	86.0
6	0.523	1.046	0.072	27.0	2.0	5.3	8.0	47.67	93.5
7	0.523	1.046	0.060	28.0	2.5	5.3	8.0	45.89	90.0

For these reasons, it was necessary to control the temperature of the reaction mixture in the range between 25-30 °C. If, however, CuO is produced, it is necessary to add a diluted solution (25 %) of sulphuric acid into the reaction mixture, which dissolves impurities by formation of $(Cu(H_2O)_6)^{2+}$ ions, as shown in equation (6):

$$CuO_{(s)} + 2H_3O^+_{(aq)} + H_2O_{(l)} = (Cu(H_2O)_6)^{2+}_{(aq)} \qquad (6)$$

Upon addition of sodium carbonate this ion produces copper(II) carbonate which subsequently reacts with sodium hydroxide resulting in copper(II) hydroxide formation. In that way, in case of tapping the system from stationary work, it is possible to transform generated copper(II) oxide into copper(II) carbonate by applying the simple presented methodology.

The results of analysis of copper(II) hydroxide products obtained under the experimental conditions, shown in Table 1, obtained at laboratory level is given in Table 2. All synthesis procedures were designed to obtain a product of commercial value which contains Cu^{2+} ion in the range from 55 to 60 % in the final formulation.

Table 2. Contents of copper, sulphate, carbonate, phosphate and moisture, pH values and the yield of copper(II) hydroxide under the experimental conditions shown in Table 1

Experiment	Content, %				
	Cu^{2+}	SO_4^{2-}	PO_4^{2-}	CO_3^-	Moisture
1	60.9	0.3	3.0	3.5	0.9
2	54.1	0.4	3.1	3.6	0.9
3	59.7	0.4	3.2	3.5	0.8
4	59.8	0.3	3.6	3.2	0.9
5	55.0	0.3	3.5	3.1	0.8
6	60.1	0.3	3.3	4.1	0.8
7	60.3	0.4	3.2	3.0	0.8

The obtained results, presented in Table 3 indicate that the most favorable range of parameters of synthesis are: an equimolar ratio of reactants $CuSO_4 \cdot 5H_2O:NaOH:Na_2CO_3 = 1.0:2.0:0.125$, reaction temperature 25-30 °C, reaction time of 2 hours, and pH-value of the suspension controlled in the range 7.5-8.5. The resulting suspension content of copper(II) hydroxide was adjusted in the final suspension to be in the range from 5.0 to 6.0 %. In synthesis processes at laboratory conditions this parameter was found to be in the range 5.3-5.5 %. This operational parameter was adjusted in order to achieve better reactor productivity at industrial conditions, which ultimately defines the physical volume of production for one batch. Further, the percentage of suspension in the product obtained, i.e. in the reaction mixture at the end of the reaction, is very important for continuous filtration using the Oliver filter in the industrial production. Adaptation of the laboratory synthesis, where more concentrated suspensions are easier to filter with less water needed for filter cake for removal of sulphates, was performed with the aim to adjust operational feasibility at the industrial level. It was found that the most economical approach was to obtain the product at 5.0-6.0 % aqueous suspension at the end of reaction. At higher concentrations, density of the reaction mixture increased rapidly, which prevented efficient mixing resulting in an inhomogeneous product.

Considering presented results, it could be concluded that the obtained product was of a good quality indicating that the technology could be implemented at the industrial level. The content of copper was within of the optimal limits, which is important from the point of view of the application as a finished commercial product. Emulsifier and dispersant, Tensiofix LX Special and Supragil WP, respectively, and kaolin filler were added in the range from 15 to 17 % to the formulated product.

The percentage of copper in the products obtained is quite uniform (Table 2), except in the experiment **5**, where the excess sodium hydroxide was used, as well as in the experiment **2**, where the reaction was performed at an elevated temperature. In these cases, copper(II) oxide was formed, which is undesirable in the final product, so that the resulting solids from these two experiments cannot be further used without additional processing. Contents of phosphate, carbonate and sulphate were optimal in all experiments, indicating that the obtained filter cake can be further dried to decrease moisture content to less than 1 %. Results of FTIR analysis of copper(II) hydroxide obtained in the experiments **1-7** confirmed successfulness of the synthesis process. Bands at 700 cm^{-1} and 3426 cm^{-1}, originating from the Cu-O and O-H stretching vibrations, respectively, were observed.

Copper(II) hydroxide is thermodynamically unstable, and partial decomposition occurs as a result of inadequate synthesis conditions, impurities, and ambient conditions/exposure to factors which influence this transformation. Increased temperature is a well-known factor which contributes to promotion of the decomposition of copper(II) hydroxide to copper(II) oxide. Weiser *et al.* [31] reported that under otherwise constant conditions, the rate of transformation of copper(II) hydroxide to copper(II) oxide is higher, the smaller the crystals of copper(II) hydroxide are. The authors also found that copper(II) hydroxide gels, prepared by addition of alkali in a slight excess to a cupric salt solution, decompose even at room temperature and even a trace of alkali accelerates the decomposition [31]. In the present study, copper(II) hydroxide was stabilized using water-soluble phosphate, which was mixed with water dispersion containing the product under mechanical stirring (by a propeller or turbine type stirrer) to ensure good homogenization. The materials can be combined in any order applicable at installed equipment, but mixing may be facilitated by adding the copper(II) hydroxide to a water-soluble phosphate. The water-soluble phosphate could be fully or partially dissolved in water before adding the copper(II) hydroxide. Generally, it is preferred to achieve complete dissolution prior to copper(II) hydroxide addition to ensure efficient copper(II) hydroxide particle surface treatment/surface reaction (precipitation at the molecular level) without reactant residues in solution. Also, efficient agitation/mixing of the reaction mixture in the course of addition provides good contact between copper(II) hydroxide particles and water-soluble phosphate to obtain minimal phosphate coverage at the highest stabilization effect. The stabilization of copper(II) hydroxide was performed mostly at ambient temperature, *i.e.* in the range from 20 to 25 ^oC, as the most convenient [32].

Because of these facts, at the end of the reaction, a solution of phosphoric acid was added in an equivalent amount to ½ of the portion of sodium hydroxide 1.046/2 (0.523 mol), whereby the sodium phosphate played the role of stabilizer in the final product.

Results of optimized laboratory procedure were used in a scale-up procedure at industrial production, by performing five batch syntheses, to evaluate successfulness of technology transfer as well as reproducibility of the obtained results. Detailed description of the technology is presented in section 2.3. The quantities of reactants, used in all batches, are as follow: water 600 l (reactor of 10 m^3), 50 kg Na_2CO_3 (98 %), 3800 l of 22 % copper(II) sulphate solution (density 1.160 g cm^{-3}) (gradual addition of nine portions of 400 l, and the last of 200 l), 2000 liters of 14 % NaOH solution (density 1.153 g cm^{-3}), and 100 l of 10 % phosphoric acid solution. The contents of copper, sulphate, carbonate, phosphate amounts and moisture in the copper(II) hydroxide obtained at the industrial level, as well as in the final product - BLAUVIT are presented in Table 3.

Table 3 Results of the industrial production of BLAUVIT preparation

Batch	$Cu(OH)_2$[a]								Formulated preparation, BLAUVIT[b]				
	Content, %					pH	Yield, kg	Yield, %	Weight, kg	Cu content, %	Wetability, s	pH[d]	Bulk density, kg m^{-3}
	Cu	PO_4	CO_3	SO_4	H_2O								
1	60.8	5.7	5.6	0.8	1.42	8.4	352	92.88	420	50.1	60	8.45	418.1
2	60.5	6.4	6.3	0.8	1.72	8.3	346	91.30	425	50.3	55	8.50	420.1
3	59.3	6.2	7.1	1.5	1.37	8.4	348	91.80	423	50.2	48	8.70	422.1
4	59.0	6.6	7.5	2.8	1.51	8.3	356	94.00	419	51.0	50	8.30	420.0
5	59.5	6.6	7.9	2..6	1.39	8.1	351	92.60	421	50.7	49	8.43	419.2

[a] yield of reaction calculated according to the copper content; [b] obtained formulated BLAUVIT with copper content of 50.5±0.04 % (The difference between weight of Blauvit and $Cu(OH)_2$ are due to fillers addition such as Tenziofix LX, Supragil WP and kaoline); [c] wettability of material ready to use; [d] pH of dispersion

Based on the results shown in Table 3, it can be concluded that high yields of produced copper(II) hydroxide concentrates, as well as of the formulated BLAUVIT preparation have been obtained. According to the specification of the formulated product, which is declared as a 50±1 % copper content, precise formulations of 50.5±0.4 % have been achieved in the industrial production. Physical parameters were within the limits of the allowed values, so the synthesized preparation was commercially packaged and put up for sale. It is used in plantations of grapevine for the suppression of the causative agents of Phytophthora infestans in the concentration of 0.35 to 0.40 % (35 to 40 g per 10 liters of water).

4. CONCLUSION

The described laboratory procedure for the synthesis of copper(II) hydroxide products in this paper defines optimal reaction conditions and the obtained product is of high purity. The synthesis reaction took place in the aqueous environment under mild reaction conditions. Reproductive results of synthesis under laboratory conditions were confirmed at the industrial level. The formulated preparation, was of high quality indicating that it can be used as a fungicide and bactericide with preventive action. Based on the obtained procedure, BLAUVIT, a commercial product is distributed on the market in the form of a blue wettable powder.

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SAŽETAK

Inovativna ekološki prihvatljiva tehnologija proizvodnje bakar(II)-hidroksida

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U radu je predstavljena inovativna laboratorijska procedura za sintezu bakar(II)-hidroksida u obliku vodene suspenzije. Procedura se zasniva na reakciji između bakar(II)-sulfata pentahidrata i natrijum-hidroksida. Mehanizam reakcije se sastoji iz sukcesivne jonske izmene karbonatnih jona sa hidroksidnim jonima i odvija se u više stupnjeva. Prvi stupanj predstavlja proizvodnju bakar(II)-karbonata i natrijum-sulfata reakcijom bakar(II)-sulfata sa natrijum-karbonatom, nakon čega sledi dodavanje rastvora natrijum-hidroksida, pri čemu se proizvod, bakar(II)-hidroksid, dobija oslobađanjem ekvimolarne količine natrijum-karbonata. Potom sledi ekvimolarna reakcija bakar(II)-sulfata i natrijum-hidroksida koja dovodi do maksimalnog iskorišćenja reaktanata. Natrijum fosfat, formiran u završnoj fazi procesa dodavanjem 10 % rastvora fosforne kiseline, deluje kao stabilizator bakar(II)-hidroksida. Visok prinos proizvoda dobija se optimizacijom parametara sinteze: vremena reakcije, molarnog odnosa reaktanata i temperature reakcije, a sam proizvod je formulisan radi dobijanja komercijalnog proizvoda koji se koristi kao fungicid i baktericid.

Ključne reči: bakar(II)-hidroksid, fungicid, zaštita biljaka, sinteza