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ORIGINAL RESEARCH ARTICLE

Synthesis of copper hydroxyphosphate under the principles of green chemistry

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ABSTRACT

This work aims to present two syntheses according to the green chemistry principles of $Cu_2(OH)PO_4$. The first one is a mechanochemical synthesis which was carried out with $Cu_3(PO_4)_2$ and NaOH at room temperature and without solvent (principles five and six), the second one employed an aqueous suspension of copper phosphate (principle six). The products were characterized by X-ray diffraction, scanning electron microscopy, infrared spectroscopy and elemental analysis. Using an analysis and evaluation scale based on green principles, the synthesis method reported in this study was compared with the traditional hydrothermal synthesis method, which was found to be a polluting process, while the synthesis method reported in this study was a clean process. It was concluded that clean processes lead to time savings, low energy costs and environmental care.

Keywords: Green Metrics; Clean Processes; Energy Saving; Mechanochemistry

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1. Introduction

Copper phosphate is of scientific interest, because they exhibit catalytic activity in the oxidation of aromatic compounds[1,2], but in particular the oxhydryl-coordinated compound exhibits activity in phenol hydroxylation[3,4] and in dye oxidation[5] due to its OH-coordinated group[6]. Moreover, they are photocatalysts with hierarchical superstructures with photocatalytic activity in visible[7] and near-infrared light[8,9]. They act as synthesis controllers of various architectures and morphology-dependent 808 nm laser-driven photothermal performance[10] and impart antimicrobial properties to the materials[11]. Also, these compounds present large pores that make them useful in separation processes acting as selective agents[12] and as adsorbents. On the other hand, the preparation of nanostructured copper phosphate, has come to fill gaps in science, since they increase the catalytic and adsorption properties[13].

One of the most widely used ways for the synthesis of copper hydroxyphosphate is reported in the literature with the hydrothermal method[11]. Sierra *et al.*[14], perform the synthesis of $Cu_2(OH)PO_4$ in a reactor at moderate pressure and temperature. But nowadays, syntheses are being developed in a cleaner and more energy-saving way, so that solid-phase synthesis (mechanochemistry) and liquid-phase synthesis present products that are more environmentally friendly and prepared under the principles of green chemistry.

Green Chemistry (GC) presents a philosophy that sets high standards for conducting research and production of chemical substances and processes, maximizing their benefits and minimizing side effects that can be harmful to humans and the environment[15]. And therefore, making chemistry more friendly to health and the environment (see https://istas.net/istas/riesgo-quimico/alternativas/la-quimicaverde#more-in-section). The basic idea is to introduce in the design and development phase of new substances, products or materials that cause the least or no impact on health, the environment and reduce the risk of accidents, either by modifying the existing chemical process for a "greener" alternative synthesis or in the search for synthesizing new materials.

GC is based on 12 principles set out by Paul Anastas and John Warner in their book Green Chemistry: Theory and Practice[16].

Through design and innovation at the molecular level, GC has become a powerful tool that contributes to:

(1) Reduce the chemical risk associated with the use and manufacture of chemical products;

(2) Reduce or eliminate the environmental impact of wastewater and the dispersion of pollutants in the atmosphere;

(3) Reduce the intensive use of water and energy;

(4) Reducing the environmental impact of chemicals once used; and

(5) Minimize the flow of matter from non-renewable natural resources to production processes.

The aim of the work is to propose two syntheses more in accordance with the principles of green chemistry for copper (II) hydroxyphosphate according to principles five and six of GC[16,17], since both were carried out at room temperature and pressure, the first one was a synthesis called mechanochemical or solid-state synthesis without solvent. The second synthesis was using water as solvent. **Table 1** mentions principles 5 and 6 of green chemistry.

Table 1. Statements of principles 5 and 6 of Green Chemistry

Principle	Statement
5	**Reduce the use of auxiliary substances.** The use of substances that are not essential (solvents, reagents to carry out separations, etc.) should be avoided as far as possible and, if they are used, they should be as innocuous as possible.
6	**Decrease energy consumption.** Energy requirements will be catalogued according to their environmental and economic impact, and will be reduced as much as possible. Synthesis methods will be carried out at ambient temperature and pressure.

This paper also evaluates the green indices or indicators (color, number and category) of the green approach for the two syntheses reported here. **Figure 1** shows the mixed methodological tool used for the evaluation: qualitative in the ordinal category and through a color code; and quantitative, through a Likert-type numerical scale (1–10) ranging from totally brown (1) to totally green (10)[18].

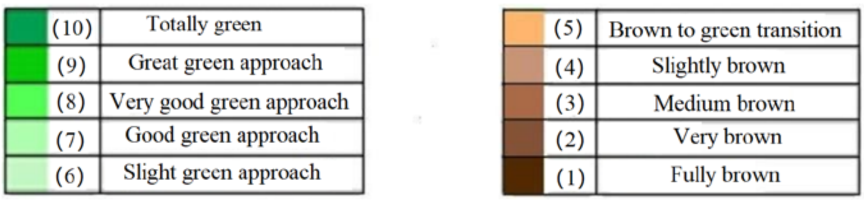

Figure 1. Color code, numerical scale and category. Tool for analysis and evaluation of a chemical process or reaction based on the principles of Green Chemistry.

Each category is applied, at the discretion based on the safety data sheets, the NFPA (National Fire Protection Association) diamond and the pictograms corresponding to toxicity, flammability, corrosion and environmental damage, of the substances involved at each step of the synthesis **Figure 2**, arranged in a flow chart.

The global evaluation is made by adding the numerical category of each principle (number in parentheses) divided by the number of them. Finally, the result is presented at the bottom of the experimental flow diagram, on the Likert-type scale of numerical assignment and corresponding color, evaluation justified in the principles of Green Chemistry[19,20].

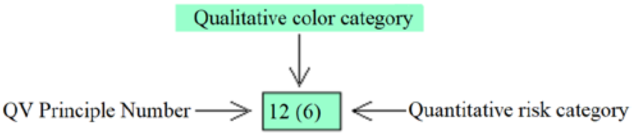

Figure 2. Green index. As an example, the evaluation of principle 12 in a reaction step with (6) Slightly green approach.

2. Materials and methods

For the synthesis of copper hydroxyphosphate under the principles of green chemistry two syntheses are presented:

(1) Mechanochemical synthesis: In a beaker with 1 gram of $Cu_3(PO_4)_2$ was slowly added and mixed with a glass rod a stoichiometric excess of powdered NaOH, the powder was added in small portions each time with gentle mixing until the color changed from light blue to military green. It was washed several times with water, filtered and left to dry at room temperature and one day in the desiccator.

$$2Cu_3(H_2O)_3(PO_4)_{2(s)} + 3NaOH_{(s)} \rightarrow$$
$$3Cu_2(OH)PO_{4(s)} + Na_3PO_4 + 6H_2O + \text{calor}$$

(2) Solvent synthesis: In an Erlenmeyer, 1 gram of $Cu_3(PO_4)_2$ suspended in 10 mL of water was mixed and a stoichiometric excess of NaOH lentils were slowly added, lentils are added in spaced portions and mixing with a glass rod (the reaction is exothermic) until the appearance of a green product and/or let stand 24 hours as it may take time for the product to appear. The solid was added water, filtered and washed several times with water, allowed to dry at room temperature and placed in a desiccator for one day.

$$Cu_3(H_2O)_3(PO_4)_{2(s)} + H_2O \rightarrow$$
$$\text{Suspension of } Cu_3(H_2O)_3(PO_4)_2$$
$$2Cu_3(H_2O)_3(PO_4)_2 + 3NaOH_{(s)} \rightarrow$$
$$3Cu_2(OH)PO_{4(s)} + Na_3PO_4 + 3H_2O + \text{heat}$$

Figure 3 shows the dry reagent copper phosphate trihydrate and the reaction product copper hydroxyphosphate.

Figure 3. Erlenmeyer flask with the reagent $Cu_3(PO_4)_2{\cdot}3H_2O$. Beaker with the product $Cu_2(OH)PO_4$.

(3) Mechanochemical synthesis by mixing in a mortar: In the mortar was placed one gram of $Cu_3(PO_4)_2$ was added and mixed with a stoichiometric excess of NaOH until the color changed from blue to emerald green, but immediately began to acquire a dark brown to black color, **Figure 4**.

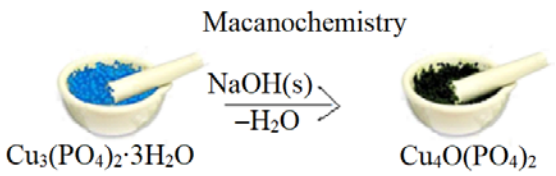

Figure 4. The reaction between copper phosphate and base in the solid state is too exothermic, dehydrating the copper hydroxyphosphate.

The dehydration reaction of copper hydroxyphosphate $Cu_2(OH)PO_4(s)$ occurs according to the following chemical equations:

$$2Cu_3(H_2O)_3(PO_4)_{2(s)} + 3NaOH_{(s)} \rightarrow$$
$$3Cu_2(OH)PO_{4(s)} + Na_3PO_4 + 6H_2O + \text{calor}$$
$$2Cu_2(OH)PO_{4(s)} + \text{calor} \rightarrow Cu_4O(PO_4)_{2(s)} + H_2O$$

Yield: For the synthesis of copper hydroxyphosphate in aqueous suspension, an excess of base was added, achieving a good precipitation, the mother waters showed a slight blue coloration. For one gram of copper sulfate, 0.908 g of copper hydroxyphosphate was obtained, which meant a yield of 91%.

For the dry synthesis of copper hydroxyphosphate, practically 1 g of copper hydroxyphosphate was obtained from one gram of copper sulfate, which meant a yield close to 100%.

In both syntheses (1) mechanochemical and (2) in water, the dry product was characterized by X-Ray Diffraction (XRD of powders) in a Philips diffractometer, by Fourier Transform Infrared Spectroscopy (FTIR) in a Varian spectrometer model Excalibur and by Scanning Electron Microscopy (SEM) with a Carl Zeiss microscope model Supra55 VP, model Excalibur and by Scanning Electron Microscopy (SEM) with a Carl Zeiss microscope model Supra55 VP and elemental analysis (SEM/EDS) with an X-ray microanalysis detector, Oxford.

3. Results and discussion

The XRD analysis of powders in **Figure 5** shows the diffractogram obtained from the copper hydroxyphosphate of the solvent-synthesized sample, together with the diffractogram of copper sulfate. The diffractogram in blue, presents diffraction peaks at angles 15, 19, 24.5, 31, 34, 37.5 and 39°corresponding to the diffraction pattern of $Cu_2(OH)PO_4$ as reported in the literature[14,21,22].

Figure 6 presents the spectra of the samples obtained by both methods, with and without solvent. The broad band between 3,500–3,300 cm^{-1} of the coordinated OH corresponds to adsorbed water and the bands at 3,571 cm^{-1} and at 1,630 cm^{-1} correspond to the vibration of the OH group to the stretching and bending modes of the hydroxyls in $Cu_2(OH)PO_4$. The bands in the region of 1,150–1,050 cm^{-1} are attributed to the asymmetric stretching ν_3 of PO_4, while the bands around 993 cm^{-1} are attributed to the symmetric stretching ν_1 of PO_4. The asymmetric bending ν_4 of PO_4 appears around 624 cm^{-1} and the symmetric bending ν_2 of PO_4 can be observed in the region of 560 cm^{-1}. In addition, the band in the range of 415–384 cm^{-1} are assigned to the vibrational bands of Cu-O in the Cu-O-P unit[21,22]. These results show that the solvothermal method is optimal for obtaining copper hydroxyphosphate.

Figure 7 shows the SEM micrographs of both the material synthesized without solvent (**Figure 7a**) and the material synthesized with solvent (**Figure 7b**). The morphology of both samples are very different, while in the sample prepared under principle five of green chemistry (without solvent) small flakes are observed tending to form clusters, in the sample prepared with solvent the morphology is well defined forming clusters with an orthorhombic prism habit of $Cu_2(OH)PO_4$ and with crystal sizes of more than 10 nm and where the presence of other morphology is not appreciated, so we can suggest that only copper hydroxyphosphate is present, as observed in the analysis of this sample by FTIR and unlike the sample without solvent where by XRD diffraction peaks were observed for both $Cu_2(OH)PO_4$ and $Cu_2(PO_4)_2$ and in the micrograph small agglomerates of a spongy material are observed between the flakes, which are probably the precursors of copper hydroxyphosphate.

Figure 8, presents the elemental analysis by SEM/EDS of the product of the synthesis with and without solvent, in the sample (a) without solvent the presence of C and Cl as contaminants is appreciated, and in the analysis of the sample with solvent (b) the theoretical percentages of each of the constituent elements have been included, which are very close to the data obtained by EDS, confirming the structure of Cu_2PO_4OH.

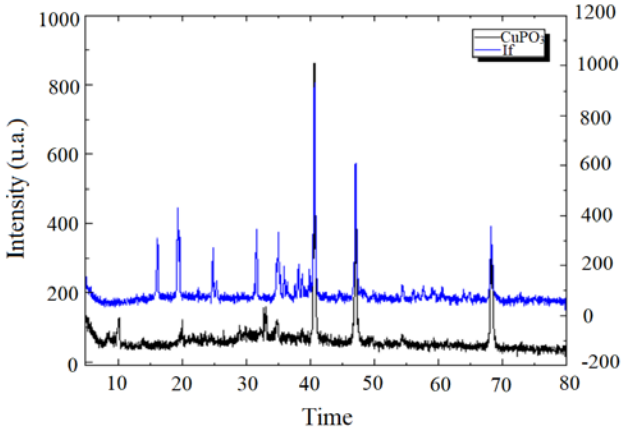

Figure 5. XRD of $Cu_2(OH)PO_4$ (blue spectrum), obtained by the solvent method, and $CuSO_4$ (black spectrum) raw material in obtaining hydroxylated phosphate.

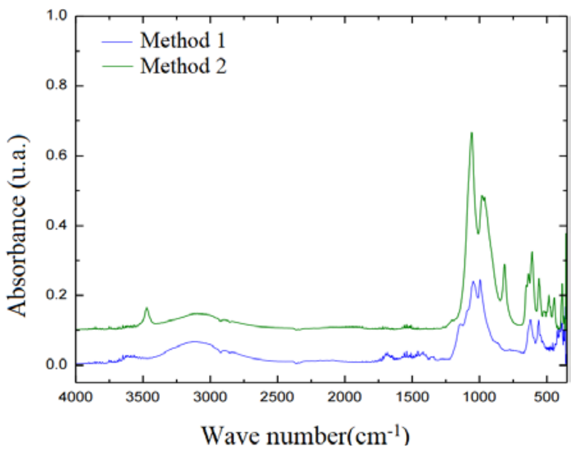

Figure 6. FTIR of $Cu_2(OH)PO_4$, obtained by the solvent-free method (method 1) in green color and with solvent (method 2).

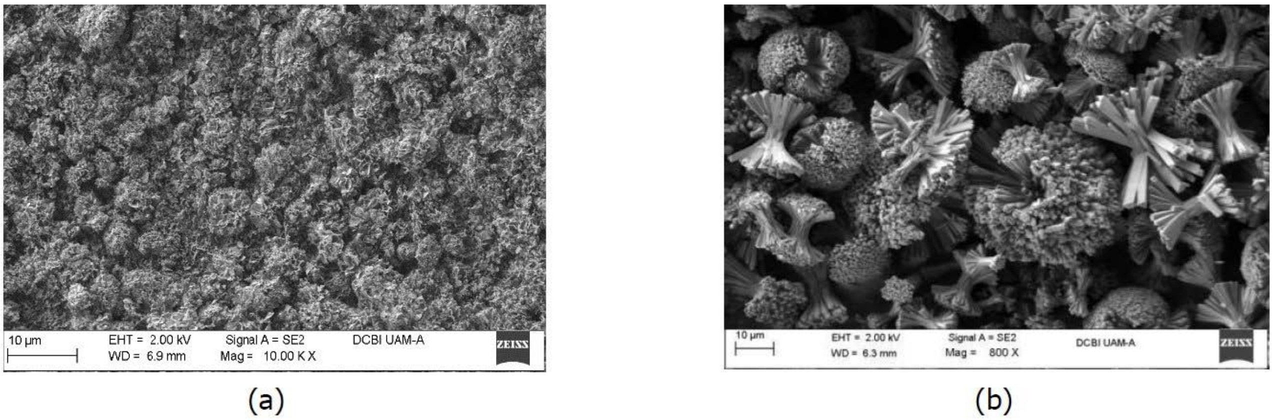

Figure 7. Micrograph of $Cu_2(OH)PO_4$; (**a**) obtained without solvent; (**b**) obtained with solvent.

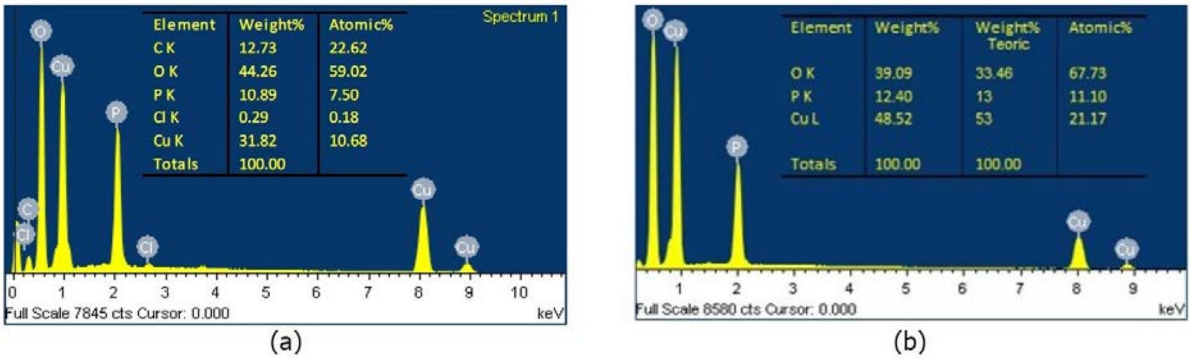

Figure 8. SEM/EDS elemental analysis of $Cu_2(OH)PO_4$; (**a**) obtained without solvent; (**b**) obtained with solvent.

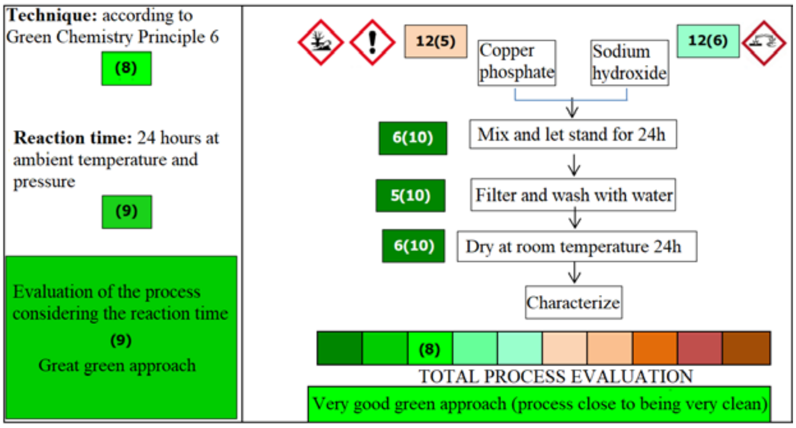

Figure 9. Flow chart (A) for the evaluation of green indices in the solvent synthesis of $Cu_2(OH)PO_4$ at room temperature and pressure. Process with large green approach.

Block diagram for the evaluation of the green indices.

The application of the green approach evaluation methodology to the aqueous phase process (A) and hydrothermal reaction method (B) of the $Cu_2(OH)PO_4$.

The analysis of the green principles and their numerical category was performed by indicating at each step the principle evaluated, the numerical, color category and the hazard pictograms of the chemicals. The final evaluation resulted by adding the numerical categories in each step between the number of principles[18].

Figure 9 shows the flow chart (A) of obtaining Cu_2PO_4OH in solution at room temperature and pressure, the analysis of green principles and its numerical category obtained was 8 and 9 when considering the reaction time of 24 hours, so the process results with a great green.

Figure 10 shows the flow diagram (B) of the hydrothermal obtaining of Cu_2PO_4OH reported in the literature[14].

The result was 4 and 2 when considering the reaction time of 50 h at temperature and pressure, therefore, the process is highly polluting.

Mechanochemistry is based on tribochemistry[23,24], which activates reactions by friction between reactant molecules that properly fuse and weaken or activate their reactive centers to bond and give new products. This methodology is in line with green chemistry, the agitation between reactive phases gives off heat and external energy savings are generated, it is performed at ambient temperature and pressure. And being an economical method at almost no cost when manuAl_2O_3 grinding is done in a mortar with pistil.

On the other hand, these methods in accordance with sustainable chemistry are suitable for obtaining nanoparticles. The synthesized products can be useful for academic scientists and industrial researchers to apply these copper phosphates in special applications such as: near-infrared activated photocatalysts[8].

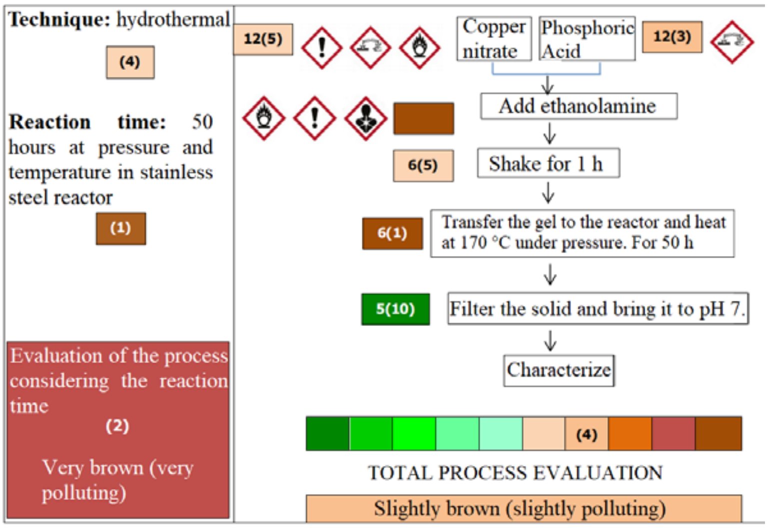

Figure 10. Flowchart (B) for the evaluation of green indices in the hydrothermal synthesis of $Cu_2(OH)PO_4$ under mild temperature and pressure conditions, resulting in a highly polluting process.

Green chemistry promotes pollution prevention at the “molecular” level. It is a paradigm of eliminating or minimizing waste generation in a chemical process.

Since the decade to educate for sustainability (2005–2014) and to date UNESCO (https://www.oei.es/historico/decada/accion004.htm) requests all educators at all levels of formal, non-formal and informal education to educate for Sustainable Development and aims to promote education as the foundation of a more viable, equitable and livable society for humanity.

Despite the successes achieved in the discipline there are still many challenges to be faced in research and development laboratories of institutes, universities and industries, so chemists must bring into play their knowledge and creativity, they must change their way of feeling, thinking and consequently act for a better social, economic and environmental welfare for present and future generations.

4. Conclusions

The mechanochemical synthesis was carried out according to principles 5 and 6 of Green Chemistry, which has the advantage of saving energy, solvent and time, with respect to the hydrothermal method, which is a conventional method of obtaining that has been reported in the literature.

The synthesis in aqueous phase with solvent presented the advantage of saving time and energy, the analysis of the green indexes and their numerical category obtained was 8 and 9 when considering the reaction time of 24 hours at pressure and room temperature, resulting in a process with a great green approach.

For its part, the hydrothermal method reported in the literature obtained a numerical category of 4 and 2, and resulted, according to the qualitative category to be very brown very polluting and requires more time and quantity of reagents than those reported in this work.

The materials obtained, both by solvent-free (mechanochemical) and solvent synthesis of copper phosphate and sodium hydroxide to obtain copper hydroxyphosphate under conditions not reported by other authors, were analyzed by X-ray diffraction, scanning electron microscopy and Fourier transform infrared spectroscopy confirming the synthesis of copper hydroxyphosphate.

Conflict of interest

The authors declared no conflict of interest.

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