STUDY OF PHOTOCATALYTIC ACTIVITY WITH SILVER AND COPPER PHOSPHATES OBTAINED BY CHEMICAL SYNTHESIS ASSISTED BY MICROWAVES

Galan Trujillo G.D., Morales Sanchez M.A., Velazquez de la Luz E., Luna-Flores A., Agustin Serrano R., Cervantes Tavera A.M., Hernández Santiago A.A.

Meritorious Autonomous University of Puebla

Puebla, Mexico.

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Abstract. Copper and silver phosphate was synthetized from chemical synthesis assisted by microwaves, which allows obtain materials in powder with time of synthesis very short. These materials are characterized by methods such as: Electronic dispersion microscopy (SEM), X-ray diffraction (DRD) and UV spectroscopy (ERDT). Their photocatalytic properties were evaluated employing methylene blue dye at a concentration of 10 ppm. The results show that these materials contribute greatly to the degradation of the dye in both cases.

Key words: *Microwave, Photocatalytic activity, Degradation, photoelectric effect.*

INTRODUCTION

The high growth in the textile industries due to its high demand which has generated a serious environmental problem, due to its toxicity, high content of chemical oxygen demand and resistance to chemical, photochemical and biological degradation. The heterogeneous photo catalysis has generated great interest due to the resolution of said problem and in turn to the conversion of solar energy. The pioneering work of Fujishima and Honda [1] has created a great study gap in materials with a high photocatalytic activity, due to its particularity of the degradation of contaminants of the textile industry, as well as the use of sunlight covering said activity in the visible region of the electromagnetic spectrum (380-780 nm) [2]. A particular material as silver phosphate (Ag_3PO_4) that has become an object of study due to its extremely high capacity for the evolution of O_2 from H_2O and the decomposition of organic dye under visible light irradiation [3]. Ag_3PO_4 has been generated by various synthesis routes such as; hydrothermal, precipitation, microwave-assisted chemistry, where the latter has given to speak because of its rapid synthesis time and the ease with which its microstructure is modified such as; branch, tetrapod, nano rod, triangular prism [4]. Another particular material is copper phosphate ($Cu_3(PO_4)_2$), which has become an interesting material due to the structural multiplicity, which gives rise to a wide variety of structures observed in ternary and quaternary phosphates, as well as silicates [5]. $Cu_3(PO_4)_2$ has been generated by conventional methods of high temperature, solid state precursors or hydrothermal techniques [6]. However the chemical synthesis route assisted by microwaves has been studied, which promises to be an effective route due to its low cost and time of preparation compared to the mentioned methods.

MATERIALS AND METHODS

The reagents used were: Ammonium acid phosphate (NH4H2PO4, from JT Baker brand), Ammonium hydroxide (NH4OH from JT Baker brand), Silver nitrate (AgNO3, from JT Baker brand), Copper nitrate (CuNO3, from JT Baker brand).

Preparation of Ag_3PO_4: Two solutions were prepared, one for silver nitrate (Solution A) and another for acid phosphate for ammonium (Solution B), in concentrations of 0.15 and 0.10 respectively, after which solution B was added to the solution A and remained in constant turmoil. The pH = 13 was adjusted with the help of ammonium hydroxide. The final solution was brought to microwave exposure for a time of 5 minutes. The solution obtained was centrifuged and washed with distilled water, the product in powder was decanted and dried for a period of 30 minutes. Finally, the material was subjected to a heat treatment of 200 ° C and a time of 30 min.

Preparation of $Cu_3(PO_4)_2$: Two solutions of copper nitrate (solution A) and another of ammonium acid phosphate (solution B), in concentrations of 0.15 and 0.10 respectively, were prepared, after which solution B was added to the solution A and remained in constant turmoil. Subsequent to this, microwave exposure was carried out for a period of 5 minutes. The final solution was centrifuged and washed with distilled water; the product was decanted and dried for a period of 30 minutes.

Photocatalytic activity evaluation: In a typical solution of methylene blue (MB) at a concentration of 10 ppm, was brought to exposure to sunlight in a batch reactor with air pumping, and with a ratio of 200 mg of catalyst per liter of solution.

The characterizations of the materials powder obtained were made by Electron Microscopy of Dispersion (SEM), X-Ray Diffraction (XDR), UV Spectroscopy (ERDT).

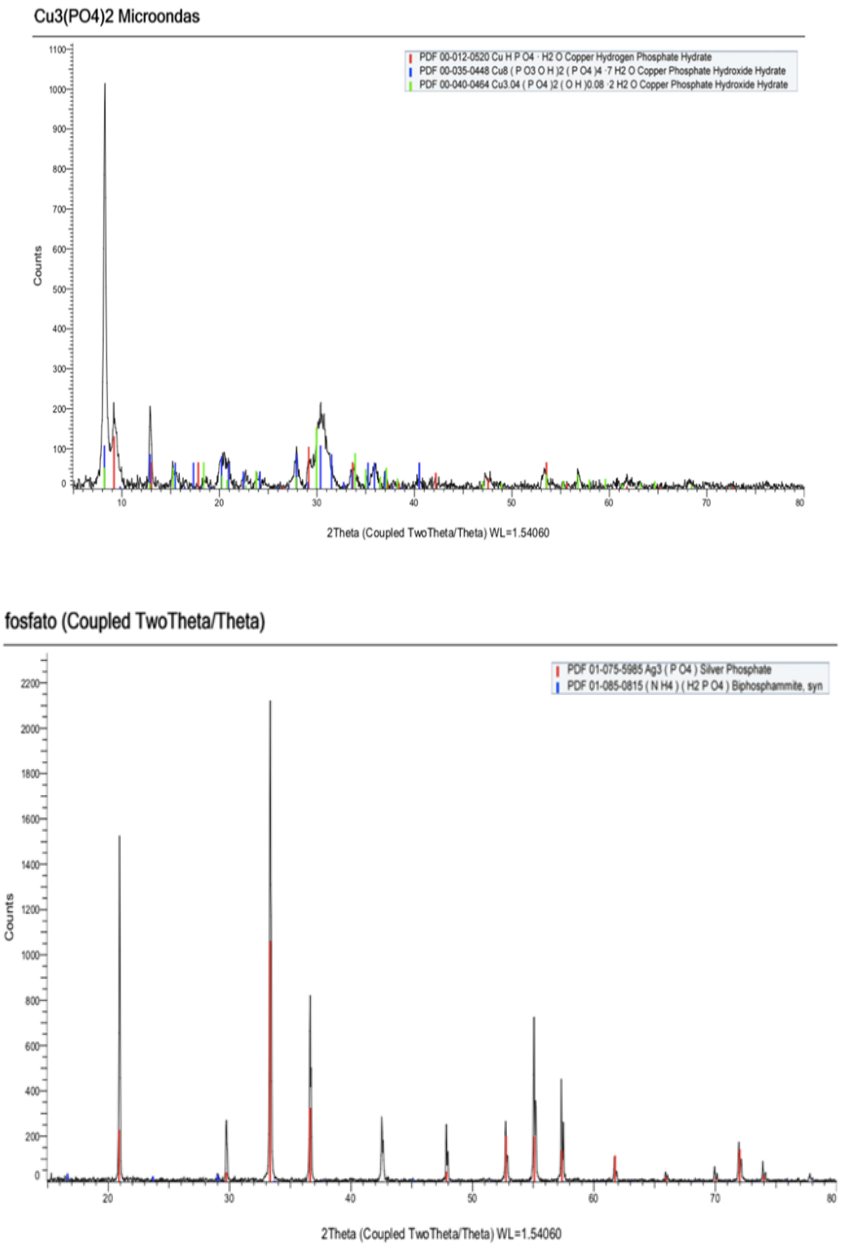

Figure 1. Left image: X-ray diffraction spectrum of $Cu_3(PO_4)_2$, right image: X-ray diffraction spectrum of $Ag_3(PO_4)$

RESULTS

The image left of Fig. 1 shows the characteristic peaks of $Cu_3(PO_4)_2$ obtained by X-ray diffraction, although, other peaks are attributed to it due to the hydration of the material. The material was obtained directly, a thermal treatment must be taken into account to improve the purity of the material, and eliminate the hydration obtained by the microwave-assisted synthesis. While the image right of figure 1 shows the X-ray diffraction spectrum of $Ag_3(PO_4)$, unlike copper phosphate, the high purity of the material can be attributed due to the increase in pH with the help of Ammonium Hydroxide.

Figure 2 shows the types of morphology reached for the case of silver phosphate, reaching a particle size in microns, where you can see cubic type, dodecahedral and some other complex morphology, which are favorable for the activity photocatalytic material. Furthermore, figure 3 shows the types of morphology obtained for the case of copper phosphate, the main morphology found are flake type. Although, there are agglomerates of particles can be attributed to the hydration of the material. This may be due to because in the case of copper phosphate the pH = 13 was not adjusted.

For the degradation tests the methylene blue dye (MB) in a concentration of 10 ppm was used, the tests were developed in solar ray capture reactors, in the figure 4 the UV spectra of the degradations with each material. For the case of $Cu_3(PO_4)_2$ for a time of 3 hours and for silver phosphate a time of 30 minutes. The difference in time is due to the great efficiency that $Ag_3(PO_4)$ has presented in the literature [7].

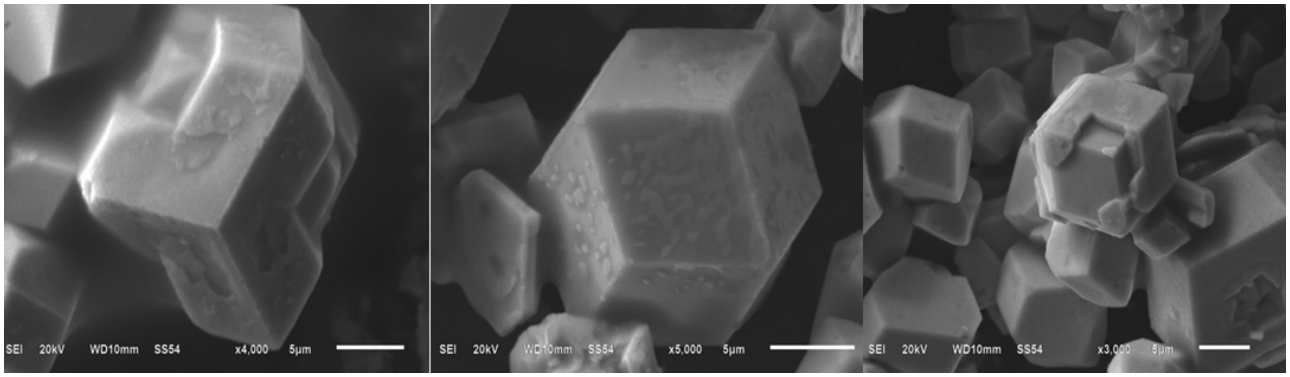

Figure 2. SEM images of $Ag_3(PO_4)$ particles whose complex crystalline habits are showed

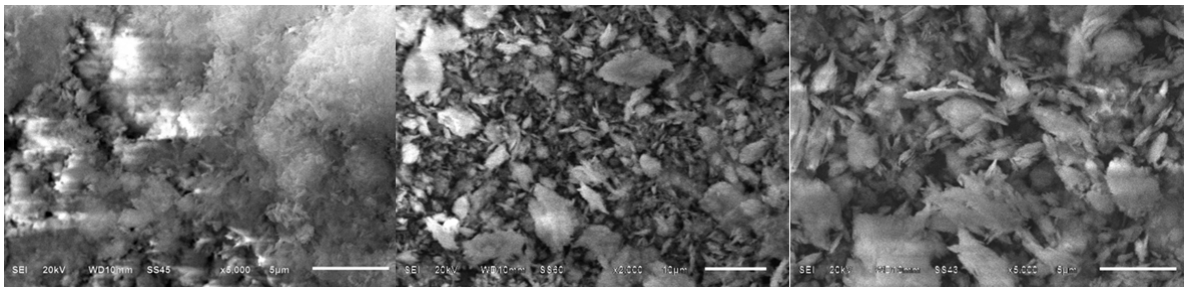

Figure 3. SEM images of $Cu_3(PO_4)_2$ particles which shows the flakes type morphology obtained

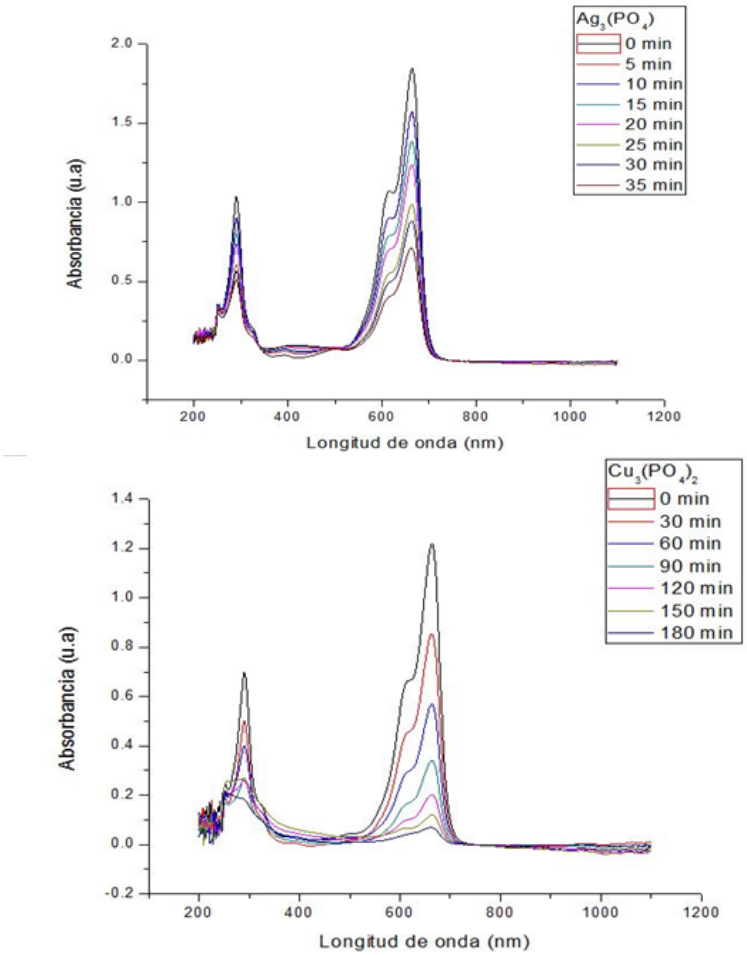

Figure 4. UV spectrum taken from degradation: left image for $Ag_3(PO_4)$ and right image for $Cu_3(PO_4)_2$

In the left image of figure 4, can be observed the degradation aliquots of the methylene blue dye in a concentration of 10 ppm for the $Ag_3(PO_4)$ powder. During the 30-minute span I reached a degradation of 41.55%. This taking into account that no type of lamp was taken, it was simply done with the help of sunlight. While in the right image of figure 4 is shows the degradation aliquots taken from the degradation of $Cu_3(PO_4)_2$ powder. This material was left for a longer time to have a closer information about the times necessary for the complete degradation of methylene blue. For comparative purposes degradation is observed at 30 min time in both cases, which is 70.34% for the $Ag_3(PO_4)$ almost double that obtained by $Cu_3(PO_4)_2$. Nevertheless, there must be more factors when comparing such as the cost of raw materials, since Silver nitrate is more expensive than copper nitrate. The synthesis time of the material $Ag_3(PO_4)$ is longer, due to its thermal treatment, in addition to the pH adjustment, which can be the key to increase the efficiency of the material.

CONCLUSION

The materials presented in this article show a desirable photocatalytic activity, although there are several points to consider, be it the cost-benefit of the raw material, the time of exposure to degradation and not using lamps to perform such tests. In general, the silver phosphate material has a better photocatalytic activity since degradation is faster in the first 30 minutes, but running degradation tests in a longer time could increase the percentage of degradation. Otherwise with copper phosphate, adjusting the pH = 13 could accelerate the photo catalysis process and thereby obtain a better photocatalytic activity.

References:

1. Fujishima A., Honda K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*, 1972, vol. 238, pp. 37-38.

2. Wang W., Lu C.H., Su M.X., Ni Y.R., Xu Z.Z. Synthesis Characterization, and Nitrogen Concentration Depended Visible-Light Photoactivity of Nitrogen-Doped TiO2 Nanosheets with Dominant (001) Facets. *Chin. J. Catal.*, 2012, vol. 33.

3. Bi Y., Ouyang S., Umezawa N., Cao J. and Ye J. *J. Am. Chem. Soc*., 2011, vol. 133, pp. 6490-6492.

4. Dong P., Wang Y., Li H., Ma X., Han L. Shape-controllable synthesis and morphology-dependent photocatalytic properties of Ag3PO4 crystals. *J. Mater. Chem. A*, 2013, vol. 1, pp. 4651-4656.

5. Etheredge K.M.S. and Hwu S.-J. A Novel Honeycomb-like Copper(II) Phosphate Framework, [BaCl][CuP04]. *Inorganic chemistry. ACS Publications*, 2019, vol. 34, pp. 3123-3125,

6. Hua Z., Li B., Li L., Yin X., Chen K. and Wang W. Designing a Novel Photothermal Material of Hierarchical Microstructured Copper Phosphate for Solar Evaporation Enhancement. *The journal of physical chemistry*, 2019, vol. 121, pp. 60-69.

7. Morales M.A., Fernández-Cervantes I., Agustín-Serrano R., Ruiz-Salgado S., Sampedro M.P., Varela-Caselis Portillo R.J.L., Rubio E. Ag3PO4 microcrystals with complex polyhedral morphologies diversity obtained by microwave-hydrothermal synthesis for MB degradation under sunlight. *Results in Physics*, 2019, vol. 12, pp. 1344-1356.