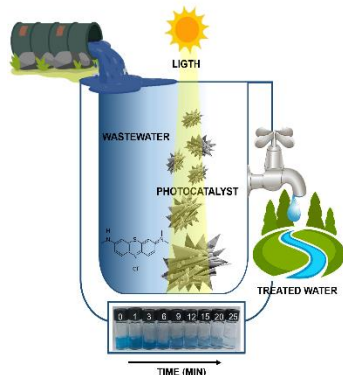


Enhanced Photocatalytic Activity of Silver Phosphate-Decorated Nickel Phosphate Microparticles Synthesized via *In Situ* Ion Exchange Reaction

POSTER
Ph.D. Student: N
Journal: CEJ

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Photocatalysis has proven to be one of the most promising advanced oxidation processes for decomposing organic pollutants from wastewater. In the present study, we report a simple and versatile synthetic route based on *in situ* ion exchange reaction to produce silver phosphate-decorated nickel phosphate $[\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2]$ microparticles with interesting photocatalytic property. In order to determine the most effective photocatalyst, different Ag/Ni molar ratios were tested in our samples. The optimized condition was found at 60 mol%, whose photocatalyst was able to degrade the methyl blue (MB) up to 25 min under blue light illumination. The photocatalytic performance of this material was tested up to three successive cycling runs. The results demonstrated that photogenerated holes (h^+) and superoxide radicals ($\text{O}_2^{\cdot-}$) were the main active species responsible for the oxidation of MB molecules.

Introduction

The humanity is facing profound challenges concerning the energy scarcity, climate change, environmental pollution and depletion of drinking water resources. These critical issues are interrelated and demand rapid action to prevent more severe implications in the future. In particular, the scarcity of freshwater is the most pressing calamity that many populations are currently experiencing in different regions of the planet. Furthermore, the quality of drinking water has been directly or indirectly affected by anthropogenic activities, which have introduced diverse pollutants as domestic sewage, pharmaceuticals, agrochemical compounds, and industrial waste [1]. The scientific community has promoted the development of different wastewater treatment techniques, including the photocatalysis. Since the pioneering study on photocatalysis published by Fujishima-Honda in 1972 [2], several semiconductors and their combinations has been studied for the decomposition of harmful contaminants in wastewater [3]. In particular, remarkable advancements have been made by using Ni and Ag-based semiconductors as photocatalysts. An interesting study was performed by Yaning et al. [4], which investigated the photocatalytic activity of heterocomposites consisting of silver phosphate $[\text{Ag}_3\text{PO}_4]$ and nickel phosphate $[\text{Ni}_3(\text{PO}_4)_2]$. Such materials were obtained through a cation exchange reaction. Firstly, $\text{Ni}_3(\text{PO}_4)_2$ was synthesized via coprecipitation, followed by the subsequent addition of silver nitrate precursor at different concentrations (40 to 80 wt. %). A similar morphological pattern was identified in all samples, revealing a high concentration of quasi-spherical Ag_3PO_4 nanoparticles well-distributed on the surface of amorphous $\text{Ni}_3(\text{PO}_4)_2$ structures. Hence, in the present study, the photocatalytic

effectivity of silver phosphate-decorated nickel phosphate $[\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2]$ microparticles was investigated for the degradation of methyl blue (MB) under blue light illumination. The *in situ* ion exchange reaction was the chosen synthetic route. For a complete analysis, the samples were synthesized with different Ag/Ni ratios in order to identify the most effective photocatalyst. All samples presented a high degree of crystallinity, with no evidence of amorphous phase. The individual contribution of reactive oxidizing species on the degradation kinetics of MB was studied by introducing selective radical scavengers into the photocatalytic reaction medium.

Material and Methods

Nickel (II) nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ (Vetec, 97%), silver nitrate $[\text{AgNO}_3]$ (Reatec, 99%), and dibasic ammonium phosphate $[(\text{NH}_4)_2\text{HPO}_4]$ (Êxodo Científica, 98%), were the starting reagents. In the first synthesis, 12 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 6 mmol of $(\text{NH}_4)_2\text{HPO}_4$ were dissolved in 120 mL of distilled water. This mixture was transferred into a stainless steel reactor. The hydrothermal treatment was performed at 160 °C for 1 h. $\text{Ni}_3(\text{PO}_4)_2$ powders were separated from the solution via centrifugation and washed. Silver phosphate-decorated nickel phosphate $[\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2]$ microparticles were prepared through an *in situ* ionic-exchange method. In this synthesis, 700 mg of $\text{Ni}_3(\text{PO}_4)_2$ was dispersed in 50 mL of deionized water. Different amounts of AgNO_3 were added to the system. The Ag/Ni molar ratios were 20, 40, 60 and 80 mol%. After stirring for 30 min, the precipitates were collected, washed and dried. Ag_3PO_4 was synthesized by coprecipitation at 90 °C for 30 min. Different experimental techniques were employed to analyse the materials, including X-Ray diffraction, ultraviolet-visible (UV-vis) diffuse

reflectance spectroscopy, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The photocatalytic activities of as-prepared samples were examined for the photodegradation of MB (10 ppm) under blue light ($\lambda_{\text{max}} = 457 \text{ nm}$). In these tests, 50 mg of photocatalyst were added in 50 mL of MB solution under constant stirring. In order to establish adsorption/desorption equilibrium between the dye molecules and the photocatalyst, the resulting suspensions were stored in the dark under constant stirring for 40 min. Afterward, the suspensions were exposed to illumination with 50W blue light-emitting diodes. The photocatalytic performance was monitored by UV-vis absorbance changes of the MB solution as a function of illumination time. The active species in the photocatalytic reaction were detected by using different radical scavengers (5 mM concentration) into the MB solution, such as isopropanol (ISO), p-benzoquinone (BQ) and diammonium oxalate monohydrate (AO).

Results and Discussion

XRD patterns of $\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2$ microparticles with different Ag/Ni molar ratios showed the coexistence of both Ag_3PO_4 and $\text{Ni}_3(\text{PO}_4)_2$ phases. Ag_3PO_4 was indexed as a body-centered cubic phase with a space group $P43n$ (ICSD no. 14000), while $\text{Ni}_3(\text{PO}_4)_2$ was assigned as a monoclinic phase with a space group $C12/m1$ (ICSD no. 240946). A gradual increase in the intensity of diffraction peaks associated corresponding to the Ag_3PO_4 phase was observed in the diffractograms. As expected, the increase in the concentration of Ag^+ ions in the ion exchange reaction promoted an increase in the fraction formed of Ag_3PO_4 , as the amount of Ni^{2+} ions was replaced. In FTIR spectra, all samples exhibited broad bands centered at 3200 cm^{-1} and 1670 cm^{-1} correspond to the stretching and deformation vibrations of the water. The absorption peak at 1005 cm^{-1} is ascribed to the asymmetric stretching vibration of PO_4^{3-} tetrahedral and 557 cm^{-1} peak is due to the asymmetric bending vibration of P–O. SEM images revealed that $\text{Ni}_3(\text{PO}_4)_2$ is composed of irregular flower-shaped microplates with an agglomerated nature. Irregular Ag_3PO_4 spheres were observed randomly distributed on the $\text{Ni}_3(\text{PO}_4)_2$ microplates (Figure 1). Therefore, the selective points located on the surface of $\text{Ni}_3(\text{PO}_4)_2$, where the exchange of Ni^{2+} with Ag^+ took place, played a fundamental role as nucleation and growth sites for Ag_3PO_4 particles.

Conclusions

The concentration of Ag^+ ions played a crucial role on the photocatalytic performance of $\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2$ for the degradation of MB. In particular, 60% $\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2$ sample exhibited the most promising photocatalytic activity, demonstrating the ability to degrade MB in 25 min. This behavior was attributed to the efficient separation of e^-/h^+ pairs due to the formation of interfaces created between Ag_3PO_4 and $\text{Ni}_3(\text{PO}_4)_2$.

Acknowledgments

Special thanks to Fundação Araucária, CNPq, CAPES, and C-LABMU/UEPG.

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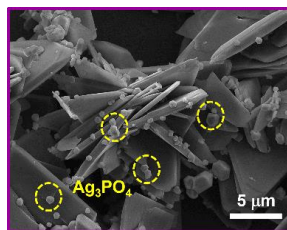


Figure 1. SEM images of 40% $\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2$. The yellow dotted circles show the presence of irregular Ag_3PO_4 spheres on the surface of $\text{Ni}_3(\text{PO}_4)_2$ microplates.

The photocatalytic activity of $\text{Ni}_3(\text{PO}_4)_2$, Ag_3PO_4 and $\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2$ samples were evaluated for the degradation of MB under blue light illumination. The degradation kinetics of $\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2$ photocatalysts was well-described by a pseudo-first-order reaction, following the Langmuir–Hinshelwood model. The experiment results indicate a synergistic effect between $\text{Ni}_3(\text{PO}_4)_2$ and Ag_3PO_4 . Such phenomenon can be attributed to the formation of interfaces that promoted an efficient pathway for the migration of photogenerated species (electron-hole) up to the photocatalyst surface. According to the reaction rate constants ($k_{\text{app}} \times 10^{-3} \text{ min}^{-1}$), the optimized photocatalysts were found in the following decreasing order: 60% $\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2$ (238) \cong Ag_3PO_4 (234) > 80% $\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2$ (167) > 40% $\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2$ (147) \gg 20% $\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2$ (35) \cong $\text{Ni}_3(\text{PO}_4)_2$ (38). In order to understand how the photodegradation reaction proceeds, different radical scavengers were introduced into the MB solution, including BQ for superoxide radical anions ($\text{O}_2^{\cdot-}$), ISO for hydroxyl radicals (OH^{\cdot}), and AO for holes (h^+). In such photocatalysts, both h^+ and $\text{O}_2^{\cdot-}$ species played a more significant role as oxidizing agents during the photocatalytic reaction (Figure 2).

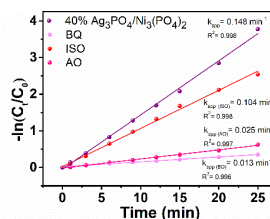


Figure 2. Pseudo-first order reaction constants for MB solution with 40% $\text{Ag}_3\text{PO}_4/\text{Ni}_3(\text{PO}_4)_2$ photocatalyst and radical scavengers.