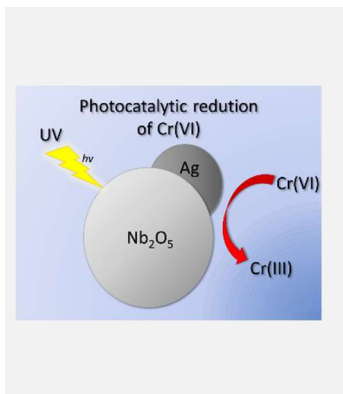


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Given the concern about Cr<sup>6+</sup> pollution, which is highly toxic, the present work presents the study of the performance of Ag/Nb<sub>2</sub>O<sub>5</sub> calcined at different temperatures in the chromium photocatalytic reduction and in different concentrations in the suspension. The results did not show a significant influence of the calcination temperature, with the catalyst calcined at 300 °C giving a slightly better result. On the other hand, the catalyst concentration had a considerable impact: increasing the concentration from 0.5 to 1.0 g/L was detrimental to the chromium reduction process.

### Introduction

Cr<sup>6+</sup> pollution causes concern due to its high toxicity and carcinogenicity compared to the trivalent form of chromium, Cr<sup>3+</sup> [1]. Among mitigation strategies, the reduction of Cr<sup>6+</sup> to Cr(III) through technologies such as photocatalysis has gained attention [2,3]. Previous work has explored using TiO<sub>2</sub> for this purpose and adding organic molecules to improve Cr<sup>6+</sup> reduction [2]. In this sense, chromium reduction, accompanied by the simultaneous reduction of various organic compounds, like benzophenone-3 [4] or 4-chlorophenol [5], has been gaining prominence. Even in simpler processes, using organic compounds acting as hole scavengers, making electron-hole recombination difficult, is fundamental [2], given the need to guarantee photogenerated electrons available for chromium reduction [6].

In this field of study, niobium-based materials have been gaining ground as an alternative to TiO<sub>2</sub>. Josué et al. and Kumar et al., for example, managed to satisfactorily reduce Cr<sup>6+</sup> using non-calcined Nb<sub>2</sub>O<sub>5</sub> [7] and Nb<sub>2</sub>O<sub>5</sub>/reduced graphene oxide nano-composite (NbO/RGO) [4] as photocatalysts, respectively.

Furthermore, impregnating metals (Au, Pd, Pt, Cu, Ni, Mg, or Ag) into photocatalysts can improve their performance [8–10]. Silver impregnation, in particular, stands out for its ability to increase photocatalytic activity and its relatively low cost compared to Au, Pd, and Pt [8–11].

Thus, the present work studied the performance of Ag/Nb<sub>2</sub>O<sub>5</sub> catalyst calcined at different temperatures (300, 500, or 700 °C) in the photocatalytic reduction of Cr<sup>6+</sup> and considering different catalyst concentrations.

### Material and Methods

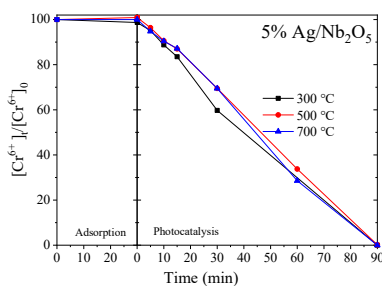
The Ag/Nb<sub>2</sub>O<sub>5</sub> photocatalysts containing 5% Ag (m/m) used in the photocatalysis tests were prepared using a straightforward method of impregnation by excess

solvent, using silver nitrate and Nb<sub>2</sub>O<sub>5</sub>, the latter kindly supplied by CBMM. The impregnation process followed the procedure described in [12].

The photocatalysis experiments were carried out using, in each test, approximately 300 mL of a synthetic chromium solution with a concentration of 20 mg/L of Cr<sup>6+</sup> with pH adjusted to 2 and with an addition of 0.01M of sodium formate in a beaker with temperature control and under magnetic stirring. At the beginning of each test, 0.5g/L of Nb<sub>2</sub>O<sub>5</sub> catalyst containing 5% silver and calcined at a given temperature (300, 500, or 700 °C) was added to the solution, which was kept in the dark for 30 minutes to evaluate the adsorption capacity of materials. After this time, a 250W mercury vapor lamp positioned over the beaker was turned on, starting the photocatalysis test. Throughout the test, samples of the suspension were collected, filtered, and stored to determine the concentration of Cr<sup>6+</sup> by UV-Vis Spectrometry (Double beam UV-VIS spectrophotometer N6000) at a wavelength of 355 nm. Catalysts characterization was performed in previous works [12,13].

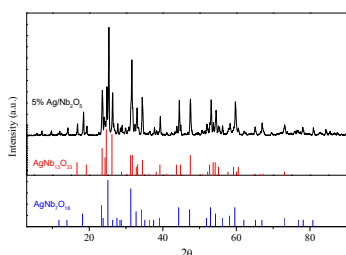
### Results and Discussion

When comparing photocatalysts calcined at different temperatures (Figure 1), similar performance was observed, being slightly superior in the case of the Ag/Nb<sub>2</sub>O<sub>5</sub> catalyst thermal-treated at 300 °C in the first 30 minutes of irradiation. Given the considerable difference in calcination temperatures in contrast to the low difference in performance, it was decided to use the catalyst calcined at 300 °C in the following tests, given that it requires lower temperatures to be prepared and, consequently, less energy and costs associated with heat treatment.



**Figure 1.** Effect of photocatalysts thermal treatment: Ag/Nb<sub>2</sub>O<sub>5</sub> calcined at different temperatures.

The XRD results, previously reported in [12], indicated the formation of AgNb<sub>7</sub>O<sub>18</sub> (PDF# 21-1084) and AgNb<sub>13</sub>O<sub>33</sub> (PDF# 21-1083) in the sample calcined at 700 °C (Figure 2), while the samples calcined at 300 °C and 500 °C probably were in the amorphous and TT-Nb<sub>2</sub>O<sub>5</sub> phase form, respectively, as observed by [7] for Nb<sub>2</sub>O<sub>5</sub> samples.



**Figure 2.** XRD results of 5% Ag/Nb<sub>2</sub>O<sub>5</sub> calcined at 700 °C [12].

## Conclusions

An Ag/Nb<sub>2</sub>O<sub>5</sub> catalyst containing 5% Ag was satisfactorily applied to chromium reduction, leading to the complete removal of Cr<sup>6+</sup> in just 90 min of irradiation. The results indicated that there was no significant benefit in increasing the catalyst calcination temperature, while increasing the catalyst concentration led to a loss in chromium reduction.

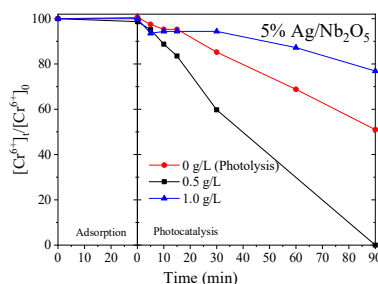
## Acknowledgments

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## References

- [1] J.J. Testa, M.A. Grela, M.I. Litter, *Environ Sci Technol*, 38, (2004) 589.
- [2] L. Wang, N. Wang, L. Zhu, H. Yu, H. Tang, *J Hazard Mater*, 152 (2008) 93.
- [3] G. Cappellotti, C.L. Bianchi, S. Ardizzone, *Appl Catal B*, 78 (2008) 193.
- [4] K.Y. Kumar, M.K. Prashanth, H. Shanavaz, L. Parashuram, F.A. Alharti, B.H. Jeon, M.S. Raghu, *Catal Commun*, 173, (2023).
- [5] J.C. Sin, S.M. Lam, H. Zeng, H. Lin, H. Li, L. Huang, K.O. A.R. Tham, Mohamed, J.W. Lim, *Environ Res*, 212 (2022).
- [6] I. Ibrahim, A. Kaltzoglou, C. Athanasekou, F. Katsaros, E. Devlin, A.G. Kontos, N. Ioannidis, M. Perraki, P. Tsakiridis, L. Sygellou, et al. *Chem Eng J*, 381 (2020).
- [7] T.G. Josué, L.N.B. Almeida, M.F. Lopes, O.A.A. Santos, G.G. Lenzi, *J Environ Manage*, 268 (2020).
- [8] X. Niu, J. Dong, X.L. Wang, Y.F. Yao, *Environ Sci Nano*, 7 (2020) 2823.
- [9] S.P. Mishra, M.R. Ghosh, *J Environ Chem Eng*, 8 (2020).
- [10] H. Eskandarloo, A. Badii, M.A. Behnajady, G.M. Ziarani, *RSC Adv*, 4 (2014) 28587.
- [11] Liu, S. Zhang, W. Zhu, P. Zuo, S. Xia, H., *J Environ Chem Eng*, 9 (2021).
- [12] G.G. Lenzi, E. Abreu, M.E.K. Fuziki, M.Z. Fidelis, R. Brackmann, J.L.D. de Tuesta, H.T. Gomes, O.A.A. dos Santos, *Top Catal*, 65 (2022) 1225.
- [13] E. Abreu, M.Z. Fidelis, M.E.K. Fuziki, R.M. Malikoski, M.C. Mastubara, R.E. Imada, J.L.D. de Tuesta, H.T. Gomes, M.D. Anzillero, B. Baldykowski, et al. *J Photochem Photobiol A Chem*, 419 (2021) 113484.

Studies were also carried out regarding the effect of catalyst concentration on chromium reduction (Figure).



**Figure 2.** Effect of photocatalyst's concentration.

The comparison of the test carried out without the addition of catalyst (photolysis) showed a considerable reduction in Cr<sup>6+</sup>. Even so, the curve referring to the concentration of 0.5 g/L proves the contribution of the catalyst to the removal of Cr<sup>6+</sup>. Increasing the Ag/Nb<sub>2</sub>O<sub>5</sub> concentration to 1g/L, however, proved a decrease in the Cr<sup>6+</sup> reduction efficiency. Probably, very high concentrations of catalyst prevent the penetration of radiation into the reactive medium, impairing photolysis and photocatalysis. The present result showed a completely different trend from that reported by Josué et al. [7], who obtained an increase in chromium reduction with an increase in catalyst concentration from 0.5 g/L to 1.5 g/L .