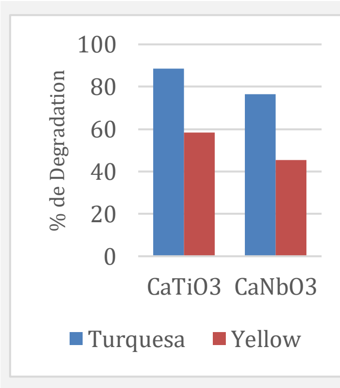
Synthesis and use of perovskites in the heterogeneous photocatalysis process

ORAL/POSTER
Ph.D. Student: Y/N
Journal: NONE

A. C. Prodocimo[1], *J.E.C. Savoia*[1], *A. M. C. Ferrari*[1], *V.A. Ribeiro,*[1] *C.D. M. Nickel*[1], *R.G. Marques*[1] *(1) Federal Technological University – Paraná, Rua Marcílio Dias, 635, 86812-460, Apucarana, Brazil, aprodocimo7@gmail.com*



Dye is one of the main effluents the textile industry generates and is classified as a difficult-to-degrade and highly toxic compound. Heterogeneous photocatalysis is one of the most widely researched advanced oxidative processes for treating this waste. Therefore, this work aimed to synthesize calcium titanate and niobate perovskites using eggshell as the calcium source and a calcination temperature of 800 ºC, and then used them to carry out photocatalysis tests to verify the photocatalytic properties of these perovskite minerals. Photocatalysis tests using UV radiation proved the photocatalytic activity of the perovskites in dye degradation, for the yellow dye the % of degradation was 58.4% for $CaTiO_3$ and 45.4% for $CaNbO_3$ and by the turquoise dye was 88.6% for $CaTiO_3$ and 76.5% for $CaNbO_3$. Thus, proving the efficiency of perovskites as photocatalysts.

Introduction

As a result of the consequences faced by modern society due to environmental contamination, there has been increasing research and development of technologies to reduce and treat industrial waste that causes environmental impacts. However, some of these wastes still have problems related to adequate and efficient treatment processes, as is the case with recalcitrant wastes, which are organic compounds that are difficult to degrade and have high chemical and photochemical stability and a slow biodegradation rate (NOGUEIRA; JARDIM, 1998). Advanced oxidative processes (AOPs) are one of the processes under development that are attracting significant interest because they are sustainable in the long term. In particular, heterogeneous photocatalysis works by activating a photocatalyst with an energy source (sunlight or artificial light) to degrade organic contaminants (NOGUEIRA; JARDIM, 1998).
Among the photocatalysts used, TiO_2 is the most commonly found in the literature due to its photoactivity and photostability. However, tests have been carried out on new types of catalysts in search of greater efficiency and lower costs. That is the case with perovskite materials due to their growing use in solar panels and their efficiency of more than 25%, have attracted the attention of researchers to explore the photocatalytic properties of these ceramic materials (DUBOSE; KAMAT, 2022).
Calcium titanate ($CaTiO_3$) was the first mineral oxide to be discovered by Gustav Rose and named Perovskite by mineralogist Lev Perovski. Thus, perovskite structures are minerals that have the chemical formula ABX_3, where "A" and "B" are cations of different sizes, and "X" is an anion that is attached to both. The ideal perovskite structure is described as cubic. In addition, its structure is stable, with various properties and applications (ASSIREY, 2019). Due to their crystalline structure, these minerals have dielectric, ferroelectric, and superconducting characteristics (KREISEL *et al*, 2000).

Therefore, this work proposes a study of the preparation and application of two perovskites ($CaTiO_3$ and $CaNbO_3$) as photocatalysts to degrade dye solution, which is the most common industrial waste found in the north-central region of the state of Paraná.

Material and Methods

1. Preparation of $CaTiO_3$ and $CaNbO_3$ perovskites

For the synthesis of perovskites, the calcium was obtained from eggshells, which were washed, the eggshell membrane removed, dried in an oven, ground, and sieved. For calcium titanate, val Degussa titanium dioxide (TiO_2) was used and for calcium niobate, niobium oxalate was used. Titanium dioxide, calcium and ethyl alcohol and niobium oxalate, calcium and ethyl alcohol were mixed. The synthesis process was the same for both perovskites, starting with an ultrasound bath for one hour, followed by 24 hours in the oven and calcination in a muffle furnace at 800 ºC for 3 hours.

2. Photocatalysis tests

After preparing the perovskites, photocatalytic tests were carried out to test their efficiency as photocatalysts. A solution of yellow dye with a concentration of 0.001 g/ml was prepared. For each test 5 ml of this primary solution was removed and diluted with distilled water, obtaining 100 ml of solution to be used in the test. Finally, an aliquot of this solution was separated into a cuvette to be read on the UV-VIS spectrophotometer.
A turquoise dye solution was also prepared with a concentration of 0.001 g/ml, then 5 ml of this primary solution was removed and diluted with distilled water, obtaining 500 ml of solution to be used in the test.
In the beakers were added 0.1 g of each catalyst and 100 ml of diluted dye solution and left to stir for 30 min yellow dye and 60 min turquoise dye for adsorption. After this, the UV lamp was used for the photocatalysis process. Aliquots of the solution were taken every 30 minutes to be

read on the spectrophotometer so that the efficiency of the catalysts in degrading the effluent could be monitored.

Results and Discussion

The results of the photocatalytic tests are shown in Figures 1 and 2.

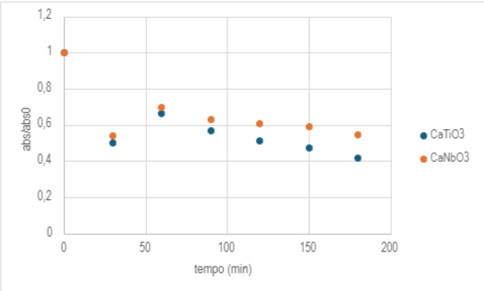
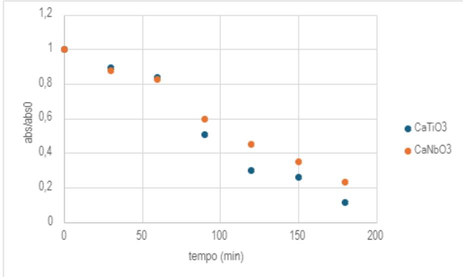


Figure 1. Photocatalyst test of yellow dye

It can be seen that the reaction behavior was different depending on the dye used. For the yellow dye, it can be seen that there was a large adsorption of dye and then it was released, increasing its concentration in the medium. After release, photocatalysis began.



.

Figure 2. Photocatalyst test of turquoise dye

It was observed that the adsorption did not have the same behavior for the turquoise dye. Being the most effective photocatalytic process.

The yield in % degradation was calculated according to equation 1.

$$\%\ \text{degradation} = \frac{Abs0 - Absfinal}{Abs0} \qquad (1)$$

Therefore, it appears that both perovskites degraded both the dyes (graphical abstract), with % degradation at the end of the test for the yellow dye of 58.4% and 45.4% and for the turquoise dye of 88,66% and 76,55% these results for $CaTiO_3$ and $CaNbO_3$, respectively. The pH of the solutions was also measured; the dye solution without catalyst had a pH of 6 and at the end of the test the solution with the titanate had a pH of 8 and the one with the niobate had a pH of 10.

Conclusions

It was observed that for the yellow dye, adsorption was a decisive factor in the reaction. In contrast, for the turquoise dye, adsorption did not have a major influence on the degradation. It was found that both perovskites have potential for application in photocatalysis.

Acknowledgments

For Araucaria Foundation and UTFPR for financial support.

References

[1] E.A.R. ASSIREY. Perovskite synthesis, properties and their related biochemical and industrial application. *Saudi Pharmaceutical Journal*, 27 (2019). Disponível em: https://www.sciencedirect.com/science/article/pii/S1319016419300726. Acesso em: 19 mar. 2024.

[2] J.T. DUBOSE, P.V. KAMAT. Efficacy of perovskite photocatalysis: challenges to overcome. *ACS Energy Lett*, 2022. Disponível em: https://pubs.acs.org/doi/full/10.1021/acsenergylett.2c00765. Acesso em: 07 mar. 2024.

[3] J. KREISEL *et al.* An x-ray diffraction and Raman spectroscopy investigation of A-site substituted perovskite compounds: the $(Na_{1-x}K_x)_{0.5}Bi_{0.5}TiO_3$ solid solution. *Journal of Physics: Condensed Matter*, 2000. Disponível em: https://iopscience.iop.org/article/10.1088/0953-8984/12/14/305/meta. Acesso em: 19 mar. 2024.

[4] R.F.P. NOGUEIRA, W.F. JARDIM. A fotocatálise heterogênea e sua aplicação ambiental. *Química Nova*, 21 (1), 1998. Disponível em: https://www.scielo.br/j/qn/a/s76bvqpyZMZK38CWzWFF9DR/#. Acesso em: 07 mar. 2024.