Increased photoelectrocatalytic effect of Nb_2O_5 by cathodic treatment for pesticide removal

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

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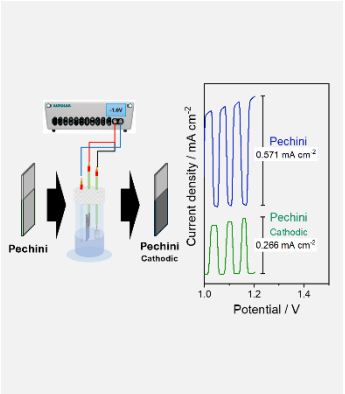

This work investigates the photodegradation of 2,4-Dichlorophenol (2,4-D) utilizing a novel approach involving a Pechini-produced Nb_2O_5 photoelectrode modified by cathodic polarization. Electrochemical treatment resulted in a remarkable increase in photocurrent from 266 to 571 µA cm^{-2}, highlighting the efficacy of the modified electrode in facilitating photoinduced reactions. Subsequent photoelectrodegradation experiments conducted over one hour demonstrated the removal of 52% of the organic molecule, underscoring the promising potential of this method for efficient pollutant remediation. The synergistic effects of cathodic polarization and Nb_2O_5 photocatalysis offer valuable insights into advancing environmentally sustainable wastewater treatment strategies.

Introduction

Electrochemical oxidation of pesticides is increasingly being used for water remediation and contamination, and it has the huge capacity to deal with eliminating pesticides from water sources. Therefore, the real-life implementation of electrochemical degradation can provide a robust solution to many problems, such as agricultural runoff, industrial discharge to the environment, and contaminated groundwater remediation [1]. This could be achieved by tailoring solutions to contamination issues with individual electrode materials, current rate, electrolyte composition, and parameters adjusted for different pesticide compositions and environmental conditions. Additionally, the multipurpose use of chemical electrode decontamination makes them appropriate for small-scale decentralized management facilities and large-scale centralized process plants and, therefore, enables the continuous batch process to combat pesticide pollution all over the globe. In addition, the use of photoactive electrodes may lead to a more efficient detoxification. Meanwhile, energy consumption and environmental impacts are altogether reduced. Moreover, the utilization of renewable resources includes solar radiation, which shows that this approach is the determination of a sustainable technology [2].

Among the mentioned methods, the present study applies Nb_2O_5 as an effective photoactive material for the degradation of 2,4-Dichlorophenol (2,4-D), an herbicide commonly used with glyphosate in large-scale fields by farmers in various countries.

Material and Methods

The electrodes were prepared using the Pechini method [3]. Initially, Ti plates were treated by sandblasting, followed by chemical etching in boiling solutions of HCl (1:1 $^{w}/_{w}$) and then in oxalic acid (10% $^{w}/_{w}$) for 30 min. The substrates were then rinsed with deionized water. In the meantime, a resin containing citric acid, ethylene glycol, and the Nb precursor ($NH_4NbO(C_2O_4)_2$) was prepared by initially dissolving citric acid in ethylene glycol at 60 ◦C. The metal salt was added to this mixture to obtain a final molar ratio of 1:4:16 of metal salt, citric acid, and ethylene glycol. Following the complete dissolution of the salt, the resulting solution was brush-painted on the Ti substrate. After each resin layer, the electrodes were initially treated at 130◦C for 30 min and later at 250◦C for 10 min. Finally, after the last layer, the electrodes were treated again at 500◦C for 10 min to eliminate all organic polymers and promote the formation of the desired oxides. 10 layers were deposited to ensure the substrate was completely covered. This sample was then called Pechini. The sample, called Cathodic, was prepared by taking the Pechini sample, placing it in a solution of 0.5 mol L^{-1} of H_2SO_4, and being polarized at -1.6 V for 10 min. Then, the electrode was left in the air for at least 6 h.

The electrochemical characterizations were carried out in an acidic aqueous medium in a 3-electrode cell with a quartz window. The light source used was a 365 nm LED lamp. The degradation was performed by applying 1.2 V versus $Ag/AgCl/KCl_{sat}$ for 1 h. The 2,4-D removal was monitored using an ultra-HPLC (Shimadzu Nexera X3).

Results and Discussion

The cathodic treatment led to a small morphological change, making the film rougher. However, it still presents the cracked clay appearance typical of electrodes obtained using the Pechini method. The roughness was obtained by atomic force microscopy, which went from 265 nm to

843 nm. The X-ray diffractograms did not suggest any structural changes, although all the peaks expected for Nb_2O_5 are present. On the other hand, the electrochemical and photoelectrochemical characterizations showed that the cathodic treatment caused slight changes in the material gap band and flat potential. Also, it noticed a change in the charge carrier's density, which means that at the microstructural level, the material's electronic properties may have changed minimally.

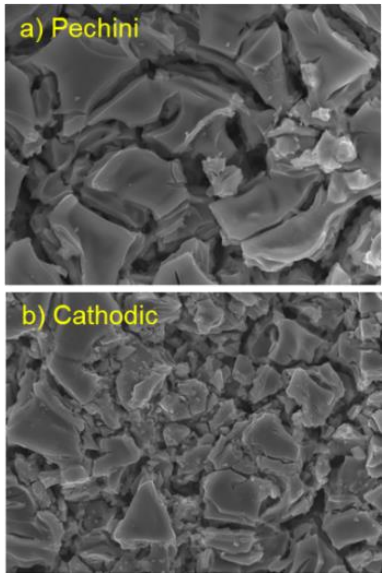

Figure 1: Scanning electron microscopy images of a) Pechini and b) Cathodic samples.

However, the photocurrent observed the biggest change, showing a substantial increase (from 266 μA cm2 to 571 μA cm2). Such an increase may be related to the joint changes observed in the morphology, with an increase in film roughness due to cathodic doping leading to a slight modification of the material's electronic structure.

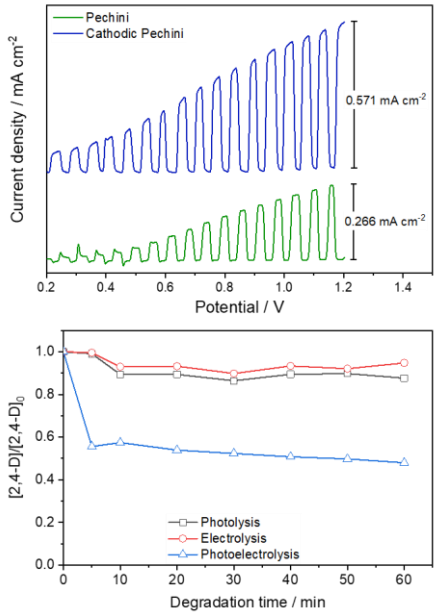

Figure 2: a) On-off linear voltammetry at a scan rate of 50mV s-1, b) Degradation curves as a function of time for the 2,4-D photolysis, electrolysis, and photoelectrolysis methods.

Thus, the material was applied to degrade 2,4-dichlorophenol, demonstrating promising results. In 1 h of photoelectrochemical degradation, 52.1 % of the pesticide was removed.

Although the removal was not as high, the material shows promise and deserves to be studied further and investigated for the mineralization of organic molecules.

Conclusions

Cathodic treatment appears to be an efficient method for improving photocurrent. It is stable enough to be applied as a material for photodegradation of an emerging pollutant such as 2,4-D. The removal of the molecule was satisfactory, suggesting that the removal would be complete in a longer time or under optimized conditions.

Acknowledgments

The authors are grateful to the São Paulo State Research Foundation (FAPESP, grants #2013/07296-2 and #2023/11548-9), CNPq (grants #465571/2014-0 and #311769/2022-5) and CAPES (code 001).

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