Photocatalytic degradation of atenolol with Nb and Ti-based supported nanocatalyst and doped with phosphorus

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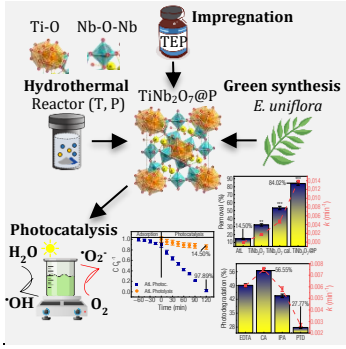

The present work aims to synthesize and characterize a Ni and Ti-based supported nanocatalyst ($TiNb_2O_7$) and doped with phosphorus ($TiNb_2O_7$@P) for the photodegradation of atenolol drug (AtL) under visible irradiation. $TiNb_2O_7$@P denoted crystalline phases of titanium niobate and phosphorus pentoxide, pH_{ZCP} of 6.45 and a negative surface charge of -17.3 ± 2.20 mV. The ideal condition by CCRD 2^2 was [$TiNb_2O_7$@P] 1.20 g L^{-1}, pH = 10 and T = 298.15 ± 2 K with degradation of 87.53% (k = 0.0210 min^{-1}) and photocatalytic stability after 5 cycles. The electron scavenger studies indicated the (e^-_{BC}) scavenger of the conduction band in the AtL photocatalysis process. Therefore, it was possible to synthesize a nanocatalyst doped with P_2O_5 denoting great potential for wastewater treatment under visible radiation, specifically the AtL drug.

Introduction

When organic compounds, such as drugs, are improperly disposed leads to environmental pollution in wastewater and soil, inhibiting local flora and fauna requiring advanced water treatments [1]. Thus, the generation of free radicals (mainly $^{\bullet}OH$ and $O_2^{-\bullet}$) through an energy-activated catalyst promoting oxidation-reduction reactions mineralizing organic pollutants is well-known as Advanced Oxidative Processes (AOPs). Typically, titanium (Ti)-based oxides are considered a prominent alternative to use in the photodegradation of organic pollutants due to their high theoretical capacity, high structural and chemical stability, notably titanium niobate $TiNb_2O_7$ which involves the transfer of five electrons (Ti^{4+}/Ti^{3+}, Nb^{5+}/Nb^{4+}, and Nb^{4+}/Nb^{3+}) increasing the generation of oxidative radicals [2]. In this context, a phosphorus pentoxide doped nanocatalyst ($TiNb_2O_7$@P) was synthesized by green synthesis/hydrothermal and impregnation method, characterized, and tested on photodegradation of atenolol (AtL) under visible radiation.

Material and Methods

1) Synthesis: $TiNb_2O_7$ was synthesized by green synthesis/hydrothermal method, where the *E. uniflora* extract (13.6 g L^{-1}) was used for reduction and nucleation followed by stabilization in a reactor stainless-steel autoclave (453.15 K for 720 min) [2]. The impregnation method was used for doping with 10 wt.% of P^{5+} ions, where triethyl phosphate was added. Thus, the sample was dried (353.15 K for 720 min) and passed to calcination (1173.15 K for 120 min).

2) Characterization: The samples were analized by X-ray diffraction (XRD); Zeta Potential (ZP); and Zero Charge Point (pH_{ZCP}).

3) Photocatalytic Activity: Central Composite Rotational Design (CCRD) 2^2 was used to determine the ideal condition for the AtL photodegradation ($4x10^{-4}$ mol L^{-1}) for 120 min. The kinetic study was determined using the pseudo first-order by the Langmuir-Hinshelwood (L-H) model [3]. The effect of temperature was evaluated ranging from 288.15 - 318.15 K by the Ahrrenius and Eyring models [4]. Additionally, it was analyzed the electron scavengers and catalyst reuse.

Results and Discussion

Figure 1(a) demonstrates the crystalline phases of the samples, where $TiNb_2O_7$@P presented the monoclinic titanium niobate phase (JCPDS#: 39-1407); and the phosphorus pentoxide phase (JCPDS#: 53-1038) with crystallite size in both phases around of 29 nm, confirming the obtaining of $TiNB_2O_7$ doped with P_2O_5. Figures 1(b) and 1(c) show the pH_{ZCP} and an initial AtL photodegradation test containing the samples, where the pH_{ZCP} of $TiNb_2O_7$@P was 6.45 and ZP of -17.3 ± 2.20 mV. In this regard, the initial tests indicated that the $TiNb_2O_7$@P showed photodegradation of 84.02% of AtL possibly due to doping with P_2O_5 causing changes in the crystalline structure associated with the Z and S configuration schemes and decreasing the niobate surface energy. It is worth mentioning that the other studies on the photocatalysis of AtL used the $TiNb_2O_7$@P. Figures 1(d) - 1(g) showed the photodegradation studies of AtL using $TiNb_2O_7$@P. The ideal condition for AtZ was ([$TiNb_2O_7$@P] of 1.20 g L^{-1}, pH of 10 and T of 298.15 ± 2 K) denoting a degradation of 87.53% and the apparent rate of the pseudo first-order reaction of 0.0210 min^{-1} with the absence of AtL crystalline phases and structural maintenance of the nanocatalyst. The effects of nanocatalyst reuse in Figure 1(h) showed

photocatalytic activity and reusability after 5 cycles (V) with degradation from 86.18 to 72.73 % (k = 0.206 – 0.0124 min^{-1}). Additionally, the assay with electron scavengers in Figure 1(i) showed the lowest degradation value of 27.77 % AtL of the potassium dichromate scavenger (PTD) indicating that the main degradation mechanism is due to (e^-) associated with the different Ti^{4+}/Ti^{3+} and Nb^{5+}/Nb^{4+} ions in solution. The influence of increasing the temperature from was significantly demonstrated in Figures 1(j) and 1(k), where the increase in temperature increments the pseudo-first-order degradation kinetics of AtL from 31.61 % to 58.09 % at 308.15 K and 318.15 K, respectively. In this sense, the synthesized $TiNb_2O_7$@P denoted an E_a of 34.61 J mol^{-1}, ΔH of -4x10^{-9} J mol^{-1} (exothermic reaction), and Gibbs free energy (ΔG < 0) indicating that the process is spontaneous.

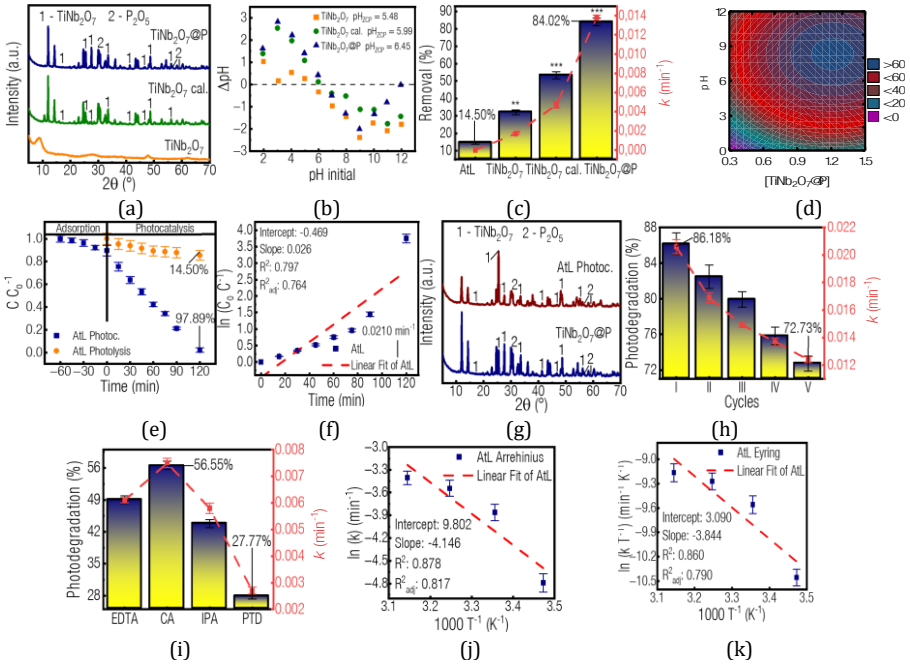

Figure 1. (a) X-ray diffractogram; (b) pH_{ZCP}; (c) Initial photodegradation tests of AtL with the samples; (d) 2D response surface; (e) Photocatalytic activity of the $TiNb_2O_7$@P in ideal condition; (f) Kinetic curve in condition ideal; (g) X-ray diffraction pattern of AtL in the ideal condition of photodegradation; (h) Effect of reuse of nanocatalyst; (i) Charged species-trapping experiments in condition ideal; (j) Arrhenius plot of ln (k) Against reciprocal T; (k) Eyring plot of ln (k T^{-1}) against reciprocal T. Statistical difference of p < 0.05*, p < 0.01**, and p < 0.001***.

Conclusions

Therefore, $TiNb_2O_7$@P showed good photocatalytic activity with potential application for atenolol removal. It is worth mentioning that the oxidative radicals formed have a lifetime of nanoseconds during heterogeneous photocatalysis promoting the recombination of the electron/vacancy pair dissipating excess energy in the form of heat and decreasing photocatalytic activity [5]. In this sense, alternatives have been adopted to avoid this possible undesirable recombination such as modifying the catalytic surface with metals and non-metals on the catalytic surface or combining different semiconductors, as well as the possibility of combining POAs.

Acknowledgments

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References

[1] Z. Mehrabadi, H. Faghihian, Comparative photocatalytic performance of TiO_2 supported on clinoptilolite and TiO_2/Salicylaldehyde-NH_2-MIL-101(Cr) for degradation of pharmaceutical pollutant atenolol under UV and visible irradiations, J. Photochem. Photobiol., A. 356 (2018) 102-111.

[2] R. Muruganantham, M.C. Lin, P.K. Wang, B.K. Chang, W.R. Liu, Highly effective Al-doped titanium niobate porous anode material for rechargeable high-rate Li-ion storage performance, *J. Taiwan Inst. Chem.* 131 (2022) 104187-104196.

[3] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, *Adv. Environ. Res.* 8 (2004) 501-551.

[4] Z. Ghasemi, H. Younesi, A.A. Zinatizadeh, Kinetics and thermodynamics of photocatalytic degradation of organic pollutants in petroleum refinery wastewater over nano-TiO_2 supported on Fe-ZSM-5, *J. Taiwan Inst. Chem. Eng.* 65 (2016) 357-366.

[5] J.A. Rengifo-Herrera, C. Pulgarin, Why five decades of massive research on heterogeneous photocatalysis, especially on TiO_2, has not yet driven to water disinfection and detoxification applications? Critical review of drawbacks and challenge, *J. Chem. Eng.* 477 (2023) 146875-146891.