Green Nb_2O_5-NPs for Rhodamine 6G photodegradation: Synthesis, characterization, phytotoxicity and photocatalytic activity

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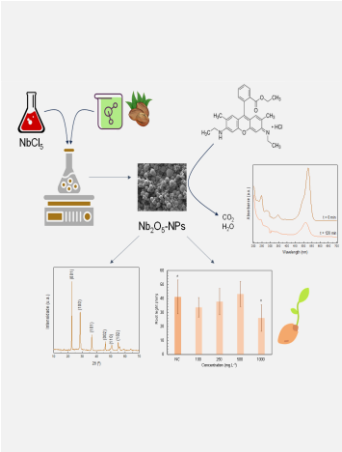

Wastewater treatment is an environmental and public health challenge nowadays. Thus, nanomaterial application in heterogeneous photocatalysis creates a new perspective for the removal of organic pollutants. In this sense, this study aims to characterize and evaluate the phytotoxicity and the photoactivity of niobium (V) oxide nanoparticles (Nb_2O_5-NPs) produced by green synthesis for the removal of rhodamine 6G (Rh 6G). The Nb_2O_5-NPs were composed of the pseudohexagonal phase, with a crystallite size of 26 nm, zeta potential of -22.6 mV and zero-point charge of 6.37. The photocatalytic test showed 75% photodegradation of Rh 6G under visible light after 120 min with a kinetic constant of 0.01256 min^{-1}. The phytotoxicity tests demonstrated inhibition in the radicular growth of *L. sativa* at the concentration of 1000 mg. L^{-1} Therefore, the green Nb_2O_5-NPs presented the potential for application in heterogeneous photocatalysis.

Introduction

Clean and safe water is an essential resource for life. However, its availability is facing challenges due to pollution of water bodies due to incorrect discharge and/or inefficient wastewater treatments to remove emerging organic pollutants (EOPs). To tackle these challenges, advanced oxidation processes (AOPs) are a promising alternative for wastewater treatment [1]. Heterogeneous photocatalysis is an AOP that attracts attention due to its versatility and regeneration capacity of the semiconductors used as catalysts. Among the different semiconductors used as photocatalysts, niobium V oxide nanoparticles (Nb_2O_5-NPs) present acidic active sites, low toxicity, and band gap energy around ~ 3.1 – 3.4 eV suitable for redox reactions [2]. Additionally, green synthesis is an eco-friendly method to synthesize nanoparticles of metallic oxides without the use of hazardous substances [3]. In this context, the presented work aimed to synthesize and characterize Nb_2O_5-NPs produced by green synthesis for photodegradation of rhodamine 6G (Rh 6G) under visible radiation.

Material and Methods

Green synthesis of Nb_2O_5-NPs

Pecan nutshells (*C. illinoinensis*) aqueous extract was used in the green synthesis of Nb_2O_5-NPs. The aqueous extract was prepared by the infusion method with 20 grams of nutshells in 1000 mL of distillate water for 10 min at 85 ± 2 °C under magnetic stirring (200 rpm). Thus, 50 mL of metallic precursor solution ($NbCl_5$ 0.1 $mol.L^{-1}$) were mixed with 50 mL of the aqueous shell extract and 5 mL of NH_4OH at 25 ± 2 °C under magnetic stirring (300 rpm / 60 minutes). The final solution was further dried at 90°C for 12h and calcinated at 500°C for 2h.

Characterization

X-ray diffraction analysis (XRD) was performed ranging from 10 – 70° in a Bruker D2 PHASER diffractometer (30 mA, 30 kV, $\lambda_{Cu-\alpha} = 0.1532$ nm). The crystallite size of the nanoparticles was calculated by the Debye- Scherrer equation and the interplanar distance by the Bragg equation [4]. The zeta potential (ZP) was used to measure the surface charge in a Malvern-Zetasizer® (ZEN3600, UK) and the zero-point charge (pH_{ZPC}) was determined by the 10-points assay test.

Phytotoxicity tests

Phytotoxicity was determined by the growth of the radicular root of *Lactuca sativa* seeds exposed to a concentration range of 100 – 1000 mg. L^{-1} of Nb_2O_5-NPs. The germination was carried out in Petri dishes with germinator paper (Germitest®) for 7 days under 23 ± 2°C and 70% humidity without the presence of light. Tukey's post hoc test was performed with a 95% confidence interval ($p < 0.05$).

Photocatalytic activity

The photocatalytic test was performed in a slurry reactor (1 g L^{-1} of Nb_2O_5-NPs) under visible irradiation (Bulb LED Lamp with 600 W m^{-2}) with a solution of Rh 6G (5 mg. L^{-1}, pH = 7) in two steps: (a) without irradiation (60 min), and (b) photocatalytic degradation of Rh 6G: under visible radiation (120 min). Thus, aliquots (~3 mL) were collected in intervals of 15 min, centrifuged (4500 rpm, 30 min) and diluted (1:10 v v^{-1}). The Rh 6G concentration was determined by UV-Vis spectrophotometry at 527 nm (Shimadzu, UV-Vis Mini 1240). The experimental data were adjusted following the Langmuir-Hinshelwood model, according to Eq. (1).

$$C_i = C_{i0} * e^{-k*t} \quad (1)$$

Where k is the apparent rate of the pseudo first-order reaction (min^{-1}); C_{i0} is the initial dye concentration (mg. L^{-1}); C_i is the dye concentration (mg. L^{-1}); and t is the photocatalysis time (min).

Results and Discussion

The Nb_2O_5-NPs diffractogram is present in Figure 1(a), where Nb_2O_5-NPs showed a crystalline structure with peaks characteristic of the pseudohexagonal phase at 22.57° ((001), 3.92 Å), 28.50° ((100), 3.12 Å), 36.66° ((101), 2.44 Å), 46.12 ° ((002), 1.96 Å), 50.63° ((110), 1.79 Å), and 55.14° ((102), 1.65 A) (JCPDS nº 28-0317). Thus, the average crystallite size and the ZP were 26.0 ± 13.8 nm and -22.6 ± 1.4 mV, respectively. Figure 1(b) shows the pH_{ZPC} plot, where is evidence that pH_{ZPC} = 6.37., when pH > 6.37 the Nb_2O_5-NPs surface is deprotonated, whereas at pH < 6.37 the surface is protonated. The photocatalytic results are presented in Figure 1(c), where the photodegradation of Rh 6G was 75% after 120 min of irradiation. The experimental data adjusted to the Langmuir-Hinshelwood model with a determination coefficient of 0.9856 and a kinetic constant of k = 0.01256 min^{-1} as presented in Figure 1 (d). The UV spectra of Rh 6G before and after the photodegradation are presented in Figure 1 (e), where the band at 527 nm in the beginning shifts after 120 min photocatalysis. These changes indicate that cleavages in the Rh 6G occurred due to the photocatalytic process. Figure 1(f) shows the results of the phytotoxicity test. Inhibition of the radicular root growth was evidenced at 1000 mg L^{-1}, indicating their phytotoxicity above this value.

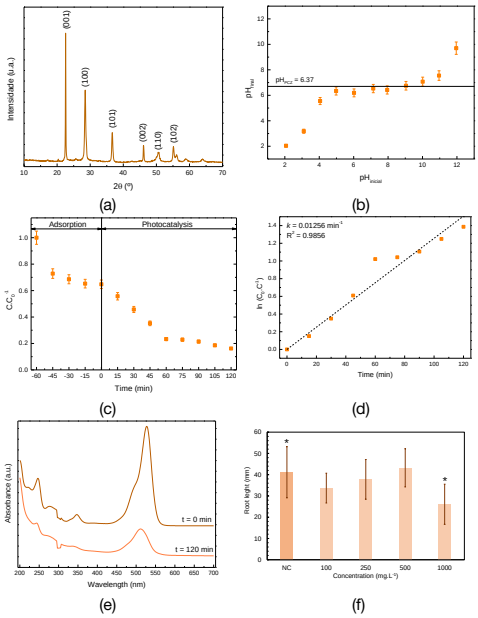

Figure 1. (a) Diffractogram; (b) pH_{ZPC} plot; (c) photocatalytic activity of Nb_2O_5-NPs for Rh 6G photodegradation; (d) linear transform ln(C_0 C^{-1}) for Rh 6G photodegradation under visible radiation; (e) Rh 6G spectra before and after the photodegradation and (f) radicular growth Nb_2O_5-NPs for *L. Sativa*.

Conclusions

Nb_2O_5-NPs presented pseudohexagonal crystalline phase with 26.0 nm crystallite size, ZP of -22.6 mV and pH_{ZPC} of 6.37. The photocatalytic tests showed the photocatalytic activity of the Nb_2O_5-NPs, with 75% of removal of Rh 6G. At 1000 mg. L^{-1} the Nb_2O_5-NPs presented inhibition on the radicular root growth of *L. sativa* seeds. Therefore, the green Nb_2O_5-NPs present prominent potential for applications in heterogeneous photocatalysis.

Acknowledgments

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References

[1] I. M. F. Cardoso, L. P. Silva, J. C. G. Silva, *Nanomaterials*, 13(2023) 1668.
[2] K. Su, H. Liu, Z. Gao, P. Fornasiero, F. Wang, *Advanced Science*, 8(2021) 2003156.
[3] A. M. Shawly, R. Elshypany, H. M. El Sharkawy, M. F. Mubarak, H. Selim, *Scientific Reports*, 14 (2024) 2456
[4] C. C. Silva, M. P. F. Graça, M. A. Valente, A. S. B. Sombra, *Journal of Materials Science*, 42 (2007) 3851.