Green Nb_2O_5 nanoparticles from *Carya illinoinensis* nutshell extract: Synthesis, characterization and photocatalytic activity for the Rhodamine B dye

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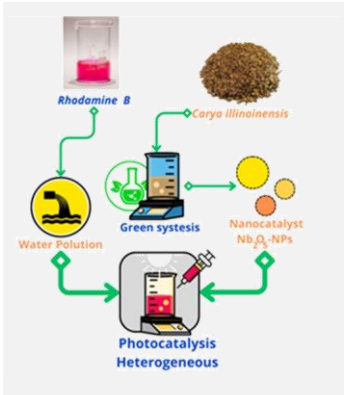

Water pollution resulting from the inadequate disposal of dyes by industry is an environmental problem. In this sense, the development of nanomaterials for application in heterogeneous photocatalysis is a promising alternative for the treatment of wastewater. In this context, the present work aims to synthesize and characterize Nb_2O_5-NPs by green synthesis from *C. illinoinensis* shell extract for the photodegradation of Rhodamine B (RhB) dye. The results showed that green Nb_2O_5-NPs are crystalline with crystallite sizes ranging from 14.5 to 31.9 nm. The surface was negatively charged (-22.7 mV), with a zero charge point of 6.77 and band gap energy of 3.25 eV. The photocatalytic tests showed the degradation of 34.6 % of RhB after 120 min under visible irradiation with a pseudo first-order kinetic behavior (k = 0.0037 min^{-1} and R^2 = 0.9963). Therefore, the green Nb_2O_5-NPs showed potetial for application in heterogeneous photocatalysis.

Introduction

The presence of synthetic organic dyes in wastewater generates several problems, such as pollution of aquatic environments and decreased photosynthetic activity. In this context, heterogeneous photocatalysis is an advanced oxidative process used in wastewater treatment, through the generation of reactive oxygen species (mainly the hydroxyl radical - ●OH), responsible for a series of oxidation-reduction reactions onto the surface of a semiconductor (photocatalyst) under the presence of irradiation (UV or visible). [1].

Niobium(V) oxide nanoparticles (Nb_2O_5-NPs) is a semiconductor with characteristics suitable for its use in heterogeneous photocatalysis, such as the availability of active sites and band gap energy (E_g) ranging from 3.0 - 3.4 eV [2].

Among the different routes to synthesize the metallic oxide nanoparticles, green synthesis is an alternative method that uses naturally bioactive compounds present in agroindustrial residues (e.g., leaves, roots and stems) that can act as reducers and stabilizers for the green synthesis of nanoparticles. In this sense, Rio Grande do Sul state (Brazil) is a major national producer of pecan nuts (*Carya illinoinensis*), generating residues such as pecan nut shells that can be used for green synthesis. Therefore, the present study aims to synthesize and characterize Nb_2O_5-NPs photocatalyst from *C. illinoinensis* aqueous extract for the Rhodamine B (RhB) photodegradation under visible irradiation.

Material and Methods

Synthesis of the Nb2O5-NPs photocatalyst

Initially, Nb_2O_5-NPs and CeO_2-NPs were prepared by the green synthesis from the *C. Illinoiensis* nutshells extract (10 $g.L^{-1}$, 85°C, 200 rpm, 10 min). Thus. 50 mL of extract were mixed with 50 mL of solution of 0.1 mol. L^{-1} $NbCl_5$ in 10% v v^{-1} of HCl, and 5 mL of NH_4OH under magnetic stirring (300 rpm, 60 min) for the reduction and nucleation steps. After, the solutions were decanted and dried (70 - 80 °C) for 12 h, followed by calcination at 600 °C for 2 h to stabilize the nanoparticles.

Characterization

X-Ray diffraction (XRD) was carried out to evaluate the crystallinities in a Bruker D2 PHASER diffractometer (10 – 70° and $\lambda_{Cu\text{-}\alpha}$ = 0,1532 nm). The crystallite size (d_c) and the interplanar distance (d) were calculated by the Debye-Scherrer and the Bragg equations [3]. The zeta potential (ZP) was determined in a Malvern-Zetasizer® (ZEN3600, UK), and the zero charge point (pH_{ZPC}) was determined by 10 point assay (pH 2 to 12) according to the literature [4]. The band gap energy (Eg) was determined by diffuse reflectance spectroscopy (JASCOV-670, 200 – 800 nm) and calculated by the Kubelka-Munk method.

Heterogeneous photocatalysis tests

The photocatalytic activity tests of the produced catalyst were performed in batch system using RhB solution (20 $mg.L^{-1}$, pH = 10) and the catalyst in suspension (3 $g.L^{-1}$) in a slurry reactor under visible irradiation (Bulb LED Lamp with 600 W m^{-2}) in two steps: (a) in dark condition: adsorption of RhB molecules onto the catalytic surface without irradiation (60 min), and (b) photocatalytic degradation of the RhB: under visible radiation, aliquots (~3.0 mL) were collected at time 0, 15, 30, 45, 60, 75, 90, 105 and 120 min, centrifuged (4500 rpm, 30 min), and diluted (1:10 v v^{-1}). The RhB concentration was determined by UV-Vis spectrophotometry at 543 nm (Shimadzu, UV-Vis Mini 1240). The experimental data were adjusted following the pseudo-first-order model (PFO) by the Langmuir-Hinshelwood model (Eq. 1).

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

Where k is is the apparent rate of the pseudo first-order

reaction (min^{-1}); C_{i0} is the initial MB concentration ($mg.L^{-1}$); C_i is the MB concentration ($mg.L^{-1}$); and t is the photocatalysis time (min).

Results and Discussion

The Nb_2O_5-NPs XRD diffractogram is presented in Figure 1(a). The Nb_2O_5-NPs presented the peaks characteristics of the pseudohexagonal Nb_2O_5 phase at 22.72° (001, d_c = 31.9 nm, d = 3.92 A), 28.60° (100, d_c = 15.5 nm, 3.12 A), 36.75° (101, d_c = 17.6 nm, d = 2.44 A), 46.22° (002, d_c = 28.7 nm, d = 1.96 A) and 55.29° (102, d_c = 14.5 nm, d = 1.65 A) (JCPDS 28-0317).

Figure 1(b) shows the pH_{ZPC}, where it was possible to verify that pH_{ZPC} = 6.77. Thus, when the pH < 6.77 the surface is protonated and pH > 6.77 the surface is deprotonated. Since RhB is a cationic dye, pH > 6.77 benefits the electrostatic interaction of the RhB molecules with the active sites of the photocatalyst, promoting greater generation of hydroxyl radicals.

The band gap energy of the Nb_2O_5-NPs was 3.25 eV according to the Tauc-plot displayed in Figure 1(c) and the surface charge of the green Nb_2O_5-NPs was negatively charged (ZP = -22.7 ± 1.7 mV).

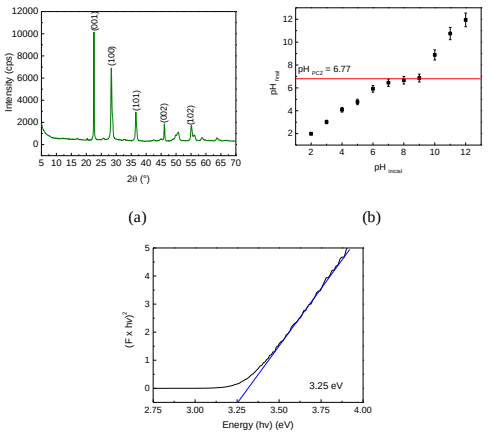

Figure 1. (a) XRD diffractogram of Nb_2O_5-NPs photocatalysts; (b) pH_{ZPC} and (c) Tauc plot of Nb_2O_5-NPs of Nb_2O_5-NPs.

The photocatalytic activity of Nb_2O_5-NPs for the RhB photodegradation is presented in Figure 2(a), and the adjustment of the experimental data to the PFO model is presented in Figure 2(b). The Nb_2O_5-NPs photodegraded 34.6 % of the RhB after 120 min under visible irradiation, with a kinetic constant obtained by the PFO model was 0.0037 min^{-1} with R^2 = 0.9963.

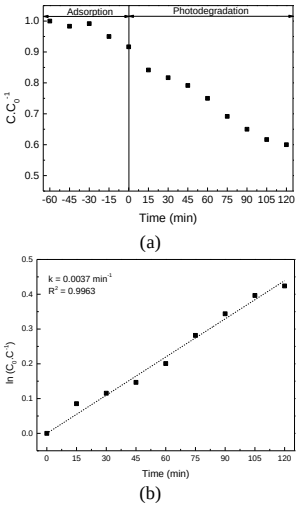

Figure 2. (a) Photocatalytic activity of Nb_2O_5-NPs under irradiation fo Rh B dye and (b) Linear transform $\ln(C_0\ C^{-1})$ for the Rh B photodegradation under visible radiation.

Therefore, the green Nb_2O_5-NPs show potential for application in heterogeneous photocatalysis. Further studies are needed to evaluated the process variables for optimization of the processes as well as the reusability of the green photocatalyst.

Conclusions

The present work reported the viability of green synthesis of Nb_2O_5-NPs using *C. Illinoiensis* shell extract. XRD diffractogram showed that the Nb_2O_5 presented peaks characteristic of pseudohexagonal phase with crystallite sizes in the range of 14.5 – 31. 9 nm. The green Nb_2O_5-NPs presented negative surface charge (- 22.7 mV), zero charge point of 6.77 and band gap energy of 3.25 eV. The photocatalytic test performed with RhB showed the photocatalytic activity of the green Nb_2O_5-NPs, achieving 34.5 % of photodegradation after 120 min. Therefore, the green Nb_2O_5-NPs present potential application in heterogenous photocatalysis. Further evaluation of the process variables are need to optimized the photocatalytic operation using the green Nb_2O_5-NPs.

Acknowledgments

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