Heterogeneous photocatalysis of organic dyes with green Nb_2O_5 nanoparticles

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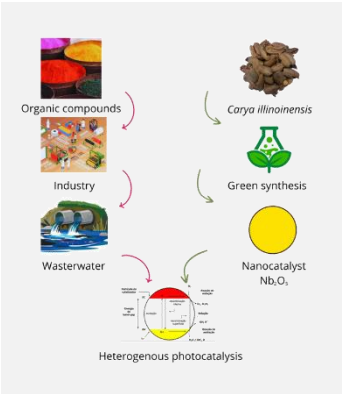

Niobium(V) oxide nanoparticles (Nb_2O_5-NPs) are an attractive type of photocatalyst for application in heterogeneous photocatalysis due to their considerable photocatalytic activity in the treatment of wastewater with dyes. Thus, the green synthesis of nanomaterials is a promising eco-friendly method, reducing the use of hazardous substances. In this context, the present work aims to produce, characterize, and evaluate the photodegradation of different organic dyes of the green Nb_2O_5-NPs using *Carya illinoinensis* shell extract. The Nb_2O_5-NPs is composed of pseudohexagonal phase, with crystallite size of 21.6 nm and a surface charge of -22.7 mV. The photodegradation test showed removal of the dyes in the range of 7.02 – 34.89%, with kinetic constants in the range of 0.0007 to 0.0034 min^{-1}. Therefore, it was possible to observe that the removal and the kinetic constant were influenced by the molecular weight of the dye, where the lower the molecular weight, the higher the removal and kinetic constant.

Introduction

The sustainability and environmental impacts caused by wastewater containing synthetic organic dyes have caused global repercussions over the years. In that regard, advanced oxidative processes (AOPs) have been applied to degrade molecules of synthetic organic dyes in wastewater due to the high removal and possibility of applying alternative nanomaterials (photocatalysts), with emphasis on heterogeneous photocatalysis [1].

Among the several types of photocatalysts, niobium(V) oxide nanoparticles (Nb_2O_5-NPs) present chemical and thermal stability, band gap energy (Eg) ranging from ~ 3.1 - 3.4 eV and low toxicity, being attractive for use in heterogeneous photocatalysis [2].

Green synthesis is an alternative method to synthesize metallic oxide nanoparticles using less toxic and hazardous substances [3]. Furthermore, the state of Rio Grande do Sul is a major national producer of pecan nuts (*Carya illinoinensis*), generating residues such as pecan nut shells. These shells presented bioactive compounds that can act as reducers and stabilizers for the green synthesis of nanoparticles. In this context, the present work aims to synthesize and characterize Nb_2O_5-NPs by green synthesis from *C. illinoinensis* aqueous extract to evaluate the photodegradation of different synthetic organic dyes under visible irradiation.

Material and Methods

Green synthesis of Nb_2O_5 nanoparticles

The green synthesis of nanoparticles was carried out using an aqueous extract of *C. illinoinensis* nutshells (10 $g.L^{-1}$, 85°C, 200 rpm, 10 min). The method was composed by the mixture of 50 mL of extract, 50 mL of solution of the metallic precursor (0.1 mol. L^{-1} $NbCl_5$ with 10% v:v of HCl) and 5 mL of NH_4OH under magnetic stirring at 300 rpm for 60 min (for reduction and nucleation steps). After, the solution was decanted and dried (70 - 80 °C) for 12 hrs. The calcination was conducted at 600 °C for 2 h to stabilize the nanoparticles.

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) to verify the crystalline structure. The crystallite size of the nanoparticles was calculated by the Debye-Scherrer equation [4] and the zeta potential (ZP) was used to measure the surface charge in a Malvern-Zetasizer® (ZEN3600, UK).

Heterogeneous photocatalysis tests

The photocatalytic tests were performed in batch mode using different organic dyes (50 mg. L^{-1} and pH 7 to the gencian violet - GV, methylene blue - MB, Rhodamine 6G - Rh 6G, Rhodamine B - Rh B, Bromocresol Green - BG and Bromophenol Blue - BB) and nanocatalyst (1 $g.L^{-1}$) in a slurry reactor under visible irradiation (Bulb LED Lamp with 600 W m^{-2}) in two steps: (a) in dark condition: adsorption of the dye molecules onto the catalytic surface without irradiation (60 min), and (b) photocatalytic degradation of the dyes: under visible radiation, aliquots (~3 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 organic dye concentration was determined by UV-Vis spectrophotometry at 582, 668, 527, 543, 615, and 588 nm for GV, MB, Rh 6G, Rh B, BG, BB, respectively (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}). (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

Figure 1 shows the XRD diffractogram of the Nb_2O_5-NPs, where presented the peaks characteristics of the pseudohexagonal Nb_2O_5 phase at 22.72° (001), 28.60° (100), 36.75° (101), 46.22° (002), 50.63° (110) and 55.29° (102) (JCPDS nº 28-0317). The crystallite size of the Nb_2O_5-NPs was 21.6 ± 8.1 nm, confirming the effectiveness of the green synthesis process of nanostructured systems.

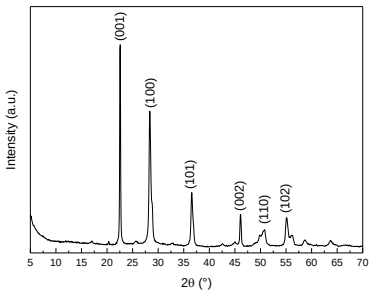

Figure 1. XRD diffractogram of Nb_2O_5- NPs.

Regarding the structural property by ZP, the nanocatalyst demonstrated a negative surface charge (-22.7 ± 1.7 mV), indicating a possible electrostatic interaction with cationic dyes (i.e., GV, MB, Rh 6G and Rh B).

The photocatalytic activity of the Nb_2O_5-NPs for the photodegradation of the organic dyes is presented in Figure 2(a). According to the experimental data, the dye photodegradation varied from 7.02 % to 34.89 % after 120 min. The adjustment of the experimental data to the L-H model is presented in Figure 2(b), where there is evidence that the values varied from 0.0007 min^{-1} to 0.0034 min^{-1} with R^2 values above 0.89.

Based on the experimental data it was possible to observe that the increase in the molecular weight reduced the photodegradation of the dye under visible irradiation as well as the reduction in the kinetic constant, as presented in Figure 3. This could be explained by the fact that the mass diffusion coefficient is influenced by the molecular weight of the target molecule. Therefore, dyes with lower molecular weights (MB and GV) presented higher removals due to the lower molecular weights compared to the other dyes (Rh 6G, Rh B, BB, BG).

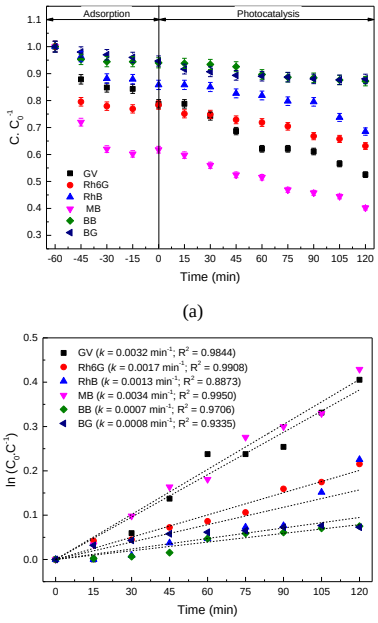

Figure 2. (a) Photocatalytic activity of Nb_2O_5 for photodegradation of organic dyes and (b) Linear transform ln(C_0 C^{-1}) for the dyes photodegradation under visible radiation.

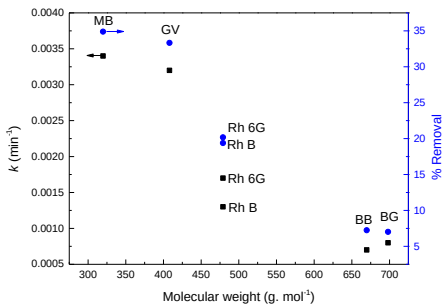

Figure 3. Influence of the molecular weight on the kinetic constant and the dye removal under visible radiation.

Further studies are needed to investigate the influence of the experimental variables (pH, catalyst concentration and dye concentration) on the removal of the organic dyes using the green Nb_2O_5-NPs.

Conclusions

The green synthesis of Nb_2O_5-NPs was possible from *C. illinoinensis* nutshells extract. XRD diffractogram showed that the Nb_2O_5 presented peaks characteristic of pseudohexagonal phases. The green Nb_2O_5-NPs presented photocatalytic activity to degrade organic dyes, where was evidenced that the higher the molecular weight of the organic dye, the lower the photodegradation under visible radiation. Further studies are needed to investigate the influence of other operational variables on the removal of the organic dyes.

Acknowledgments

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