# Effect of pH for the methylene blue photodegradation using green $Nb_2O_5$-NPs

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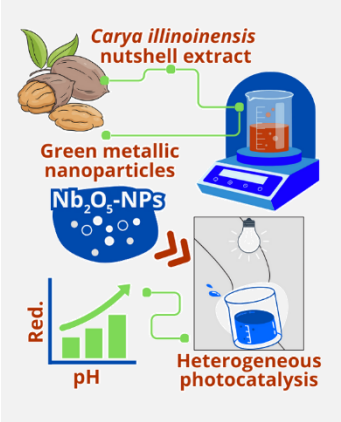



Green synthesis of metallic oxides is an eco-friendly method to produce new materials. Thus, niobium(V) oxide nanoparticles ($Nb_2O_5$-NPs) presented photocatalytic activity for application in heterogeneous photocatalysis. During the photocatalytic process, the knowledge of the influence of process variables is important to improve the photodegradation of emerging organic pollutants. In this context, the present work aims to analyze the effect of pH for the photodegradation of the methylene blue (MB) dye under visible irradiation using a green $Nb_2O_5$-NPs produced from *C. illinoinensis* nutshells extract. The results showed that the green $Nb_2O_5$-NPs presented a crystalline structure (pseudohexagonal phase) with crystallite size of 31.9 nm, a surface charge of -20.7 mV and a zero point charge of 6.77. The photocatalytic tests showed that the pH greatly influenced the MB photodegradation from 16.0 % to 60.4 % and the kinetic constant from 0.0016 to 0.0059 $min^{-1}$ when the pH changed from 4 to 10. Therefore, it was concluded that photodegradation of the MB using the green $Nb_2O_5$-$NP_S$ was favored in alkaline conditions.

## Introduction

The increase in industrialization is becoming increasingly present in the current global scenario, bringing consequences, such as the contamination of water bodies caused by incorrect discharge and/or inefficient treatment of organic dyes, pharmaceuticals, and other polluting chemicals. Thus, advanced oxidative processes (AOPs) emerged for the wastewater treatment contaminated with organic pollutants In this context, heterogeneous photocatalysis is a potential process used in the wastewater treatment, consisting of the generation of free oxygen radicals (e.g., hydroxyls and superoxide) by the photoactivation of a semiconductor under UV irradiation or visible light [1].

The application of nanocatalysts, such as niobium(V) oxide nanoparticles ($Nb_2O_5$-NPs), presents benefits in degradative processes, as this oxide is an n-type semiconductor with a band gap energy ranging from 3.0 to 3.4 eV, thermodynamically stable, which has high corrosion resistance and low toxicity [2]. Furthermore, operational variables influence the photocatalytic performance, such as the pH due to the presence of $H^+$ or $OH^-$ in the reaction medium affects the interaction of the target molecules with the active sites and the generation of oxidative species [3].

Additionally, green synthesis is an alternative method to synthesize metallic oxide nanoparticles that do not use toxic and hazardous substances. In this sense, regional residues such as pecan nut shells (*Carya illinoinensis*) have bioactive compounds that can act as reducers and stabilizers for the synthesis of nanoparticles. Therefore, the present study aimed to analyze the effect of pH in the photodegradation of methylene blue (MB) dye under visible irradiation by $Nb_2O_5$-NPs nanoparticles produced by green synthesis using *C. Illinoinensis* aqueous extract.

## Material and Methods

*Synthesis of the $Nb_2O_5$-NPs photocatalyst*

$Nb_2O_5$-NPs were prepared by green synthesis using *C. Illinoiensis* nutshells aqueous extract (10 $g.L^{-1}$, 85°C, 300 rpm, 10 min). 50 mL of extract were mixed with 50 mL of solution of the respective metal precursor (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 for 60 min) for the reduction and nucleation steps. After, the solution were decanted and dried (70 - 80 °C) for 12 h for the stabilization step. The calcination of the samples was conducted at 600 °C for 2 hours to stabilize the $Nb_2O_5$-NPs.

*Characterization*

X-Ray diffraction (XRD) was carried out to evaluate the crystallinities of heterogeneous catalysts in a Bruker D2 PHASER diffractometer (10 – 70° and $\lambda_{Cu-\alpha}$ = 0.1532 nm). The crystallite size ($d_c$) of the nanoparticles was calculated by the Debye-Scherrer equation [4] and the zeta potential (ZP) was determined by a Malvern-Zetasizer® (ZEN3600, UK). The zero point charge ($pH_{ZPC}$) was determined with ranging the pH from 2 to 12 following the literature recommendations [5].

*Heterogeneous photocatalysis tests*

The photocatalytic tests were performed in batch system using MB solution (20 $mg.L^{-1}$) with catalyst in suspension (1 $g.L^{-1}$) and evaluating the photodegradation at pH 4, 7 and 10. The reaction was conducted in a slurry reactor under visible irradiation (Bulb LED Lamp with 600 W $m^{-2}$) in two steps: (a) in dark condition: adsorption of MB molecules onto the catalytic surface without irradiation (60 min), and (b) photocatalytic degradation of the MB: 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 $v^{-1}$).

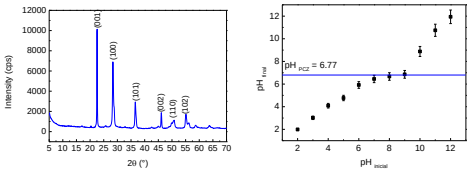
The MB concentration was determined by UV-Vis spectrophotometry at 668 nm (Shimadzu, UV-Vis Mini 1240). The experimental data were adjusted following the pseudo-first-order model (PFO) by Langmuir-Hinshelwood model, according to Eq. (1).

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

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 reaction time (min).

## Results and Discussion

Figure 1(a) shows the XRD diffractograms of the green $Nb_2O_5$-NPs, where it was possible to verify the presence of the characteristic peaks 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 28-0317). The Nb2O5-NPs presented a crystallite size of 31.9 nm and a surface charge of -20.7 mV. The $pH_{ZPC}$ was displayed in Figure 1(b), where is evidenced that the $pH_{ZPC}$ = 6.77. Therefore, when pH < 6.77 the surface is protonated and pH > 6.77 the surface is deprotonated.

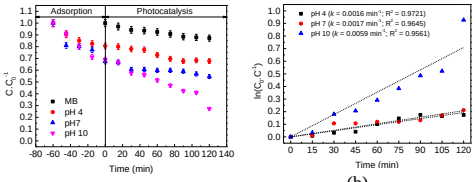



(a) (b)

**Figure 1.** (a) XRD diffractogram and (b) $pH_{ZPC}$ of the $Nb_2O_5$-NPs.

The photocatalytic activity of $Nb_2O_5$-NPs for the MB photodegradation under different pHs is presented in Figure 2(a). The removal of MB under pH 4, 7, and 10 was 16.0 %, 19.1 % and 60.4 %, respectively. This result showed that the photodegradation of MB increases in pH above the $pH_{ZPC}$, as the electrostatic attraction between the MB molecules (positively charged) is intensified and the presence of $OH^-$ species benefits the production of oxygen reactive species for photodegradation.

The linear adjustment of the experimental data to the PFO model is presented in Figure 2(b), where is possible to verify that the experimental data adjusted to the PFO model ($R^2 > 0.95$), and the kinetic constant for the pHs 4, 7 and 10 were 0.0016, 0.0017 and 0.0059 $min^{-1}$, respectively. Figure 3 shows the effect of the pH in the removal and the kinetic constant, where it was possible to verify that at pH above the $pH_{ZPC}$ the kinetic constant and the removal substantially increased.




(a) (b)

**Figure 2.** (a) Photocatalytic activity of $Nb_2O_5$-NPs for the MB photodegradation and (b) Linear transform $ln(C_0\ C^{-1})$ for the MB photodegradation.

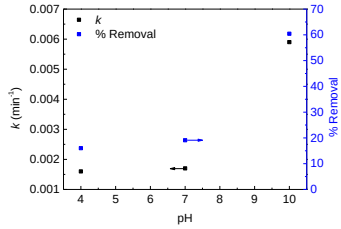



**Figure 3.** Effect of pH in the removal of MB and the kinetic constant by heterogeneous photocatalysis.

Therefore, the pH greatly influenced the photodegradation of MB by heterogeneous photocatalysis using green $Nb_2O_5$-NPs. Further studies are neeeded to evalaute other process variables (catalyst concentration and dye concentration) to improve the MB photodegradation under visible irradiation.

## Conclusions

Green synthesis were used to synthesize $Nb_2O_5$-NPs from *C. Illinoiensis* nutshells extract. XRD diffractograms showed that the $Nb_2O_5$-NPs presented crystalline structure with the presence of pseudoxehagonal phase and crystallite size of 31.9 nm. The $Nb_2O_5$-NPs presented negative surface charge (-20.7 mV) and $pH_{ZPC}$ of 6.77. The photocatalytic experiements showed that the increase in pH of from 4 to 10 the MB solution benefit the photodegradation of the target molecule using the $Nb_2O_5$-NPs as nanocatalyst from 16.0 % to 60.4%, respectively. Further studies are need to investigate other process variables to optmize the photodegradation of MB using the green $Nb_2O_5$-NPs

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