Mg^{2+} and Pt^{4+} doped $Bi_{12}TiO_{20}$ photocatalysts for photodegradation of fast green dye

POSTER
Student: N
Journal: Chemical Engineering Journal

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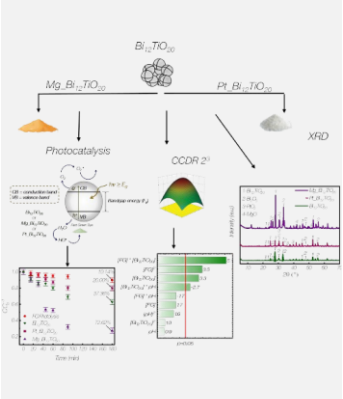

Due to contamination in wastewater by organic dyes, the present study aims to synthesize and characterize bismuth titanate nanoparticles ($Bi_{12}TiO_{20}$) from *M. officinalis* extract to evaluate the photocatalytic activity for removal of Fast Green dye (FG) under visible radiation. The nanoparticles were characterized by X-ray diffraction (XRD), Zeta Potential (ZP), and Diffuse Reflectance Spectroscopy (DRS). $Bi_{12}TiO_{20}$ presented the peaks characteristic of the perovskite and spherobismoite phases, a negative charge of -8.80 ± 4.40 mV, band gap energy (E_g) of 2.24 eV. CCRD 2^3 showed the highest dye degradation percentage at [FG] = 60 mg L^{-1}, [$Bi_{12}TiO_{20}$] = 1 g L^{-1}, pH 4. After 180 min under visible radiation. Additionally, the effect of doping with Pt^{4+} and Mg^{2+} ions was evaluated, where the doping with Mg^{2+} increased the photodegradation of FG by around 50%. Therefore, Mg^{2+} and Pt^{4+} ions doped $Bi_{12}TiO_{20}$ photocatalysts are potential catalysts in wastewater treatment with dyes.

Introduction

Contamination with synthetic dyes has been one of the main causes of environmental and socioeconomic concerns, causing unfavorable effects on the environment as an imbalance in the marine ecosystem, due to its toxicity, and on human health [1]. The fast green dye (FG) is characterized by having a high molecular weight and being chemically stable making it difficult to remove for conventional treatments requiring advanced water treatments.[2] The heterogeneous photocatalysis is based on the principle of photoactivation of a semiconductor (catalyst), under visible and UV radiation through the redox reactions with the adsorbed molecules of the pollutant on the catalytic surface. In this context, the present study aims to evaluate the photocatalytic activity of the green bismuth titanate ($Bi_{12}TiO_{20}$) from *Melissa officinalis* extract doped with Pt^{4+} and Mg^{2+} ions for the FG photodegradation.

Material and Methods

1) Biosynthesis of $Bi_{12}TiO_{20}$: Biosynthesis consists of the steps of reduction, nucleation and stabilization. Thus, 10 mL of the *M. officinalis* extract was added in a solution of bismuth(III) subnitrate (ACS, 98%, Sigma-Aldrich®) and titanium isopropoxide IV (ACS, ≥ 97.0 %, Sigma-Aldrich®) under magnetic stirring (100 rpm for 120 min). Posteriorly, the sample was centrifuged (4500 rpm for 20 min), dried (353.15 ± 2 K for 720 minutes) and calcined (1073.15 ± 2 K for 120 minutes).

2) Effect of Doping with Mg^{2+} and Pt^{4+} ions: To evaluate the effect of doping with Mg^{2+} and Pt^{4+} ions was applied the impregnation method [3], where 1 g of bismuth titanate ($Bi_{12}TiO_{20}$) was mixed with 0.02 g of magnesium chloride (2 wt.%, $MgCl_2$, powder, < 200 µm, Sigma-Aldrich®) or platinum chloride (2 wt.%, $PtCl_4$, ACS, 98%, Sigma-Aldrich®) under magnetic stirring (250 rpm and 90 min). Subsequently, the samples were dried (353.15 K for 720 min) and calcined (773.15 K for 120 min at 278.15 K min^{-1}). The resulting catalysts were labeled as X_$Bi_{12}TiO_{20}$, where X represents the dopant.

3) Characterization and Experimental Design: The samples were characterized by X-ray diffraction (XRD), Diffuse Reflectance Spectroscopy (DRS), and Zeta Potential (ZP). To determine the ideal condition for the FG photodegradation was used the Central Composite Rotatable Design (CCRD) 2^3, where the independent variables were the [FG], [catalyst] and pH, while the response variable was the percentage of dye removal (%R).

4) Photocalictic Activity: The photocatalytic activity was carried out in batch mode in 180 min under visible radiation (Bulb LED Lamp with 600 W m^{-2}) in a slurry reactor . The kinetic study was determined using the pseudo first-order Langmuir-Hinshelwood (L-H) model [4].

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

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

Results and Discussion

Fig. 1(a) shows XRD diffractograms, where characteristic peaks were identified of the perovskite phase ($Bi_4Ti_3O_{12}$ - ICDD nº 75-1149) and spherobismoite phase (Bi_2O_3 – ICDD nº 19-629). Pt_$Bi_{12}TiO_{20}$ and Mg_$Bi_{12}TiO_{20}$ demonstrated platinum(IV) oxide (PtO_2 - ICDD nº 01-078-2660) and periclase (MgO - ICDD nº01-078-0430) phases, respectively, with average crystallite size ranging from 25 - 32 nm, confirming the biosynthesis process and the doping with Mg^{2+} and Pt^{4+} ions onto the $Bi_{12}TiO_{20}$ surface. Fig 1(b) demonstrates the Pareto chart, where there was a linear interaction of the [FG] * [$Bi_{12}TiO_{20}$] and [$Bi_{12}TiO_{20}$] for the photodegradation, while the [FG] represented a positive quadratic effect, and [$Bi_{12}TiO_{20}$] * pH showed a negative linear effect. Fig. 1(c) denotes the ideal condition that was [FG] = 60 mg L^{-1}, [$Bi_{12}TiO_{20}$] = 1 g L^{-1} at pH at 4, resulting in the removal of 37.36 % after 180 min. Fig 1(d) and Fig 1(e) show that the higher removal percentage (72 %) and pseudo first-order constant (k = 0.0086 min^{-1}, R^2_{adj}=0.81) due to the doping with Mg^{2+} ions, which participate in the degradation reaction and reduce the electron-hole pair recombination, but the percentage of removal Pt^{4+} ions (20 %) and pseudo-first order constant (k =0.0016 min^{-1}, R^2_{adj}=0.88) representing an unsatisfactory result for removing. Table 1 shows the results of the ZP and E_g, where negative charges were observed for $Bi_{12}TiO_{20}$ and Mg_$Bi_{12}TiO_{20}$, indicating physio-chemical stability in aqueous solution due to the electrostatic factors. However, Pt_$Bi_{12}TiO_{20}$ showed a positive charge and poor physio-chemical stability in an aqueous solution (low ZP value). Moreover, it was observed a reduction of band gap energy of $Bi_{12}TiO_{20}$ in both doped samples (from 2.24 eV to 2.21 and 2.19 eV), which probably improved the photocatalytic activity of $Bi_{12}TiO_{20}$.

Table 1. ZP and E_g properties of the samples.

Samples	ZP (mV)	E_g (eV)
$Bi_{12}TiO_{20}$	-8.8 ± 4.40	2.24
Pt_$Bi_{12}TiO_{20}$	0.9 ± 1.45	2.21
Mg_$Bi_{12}TiO_{20}$	-11.9 ± 0.61	2.19

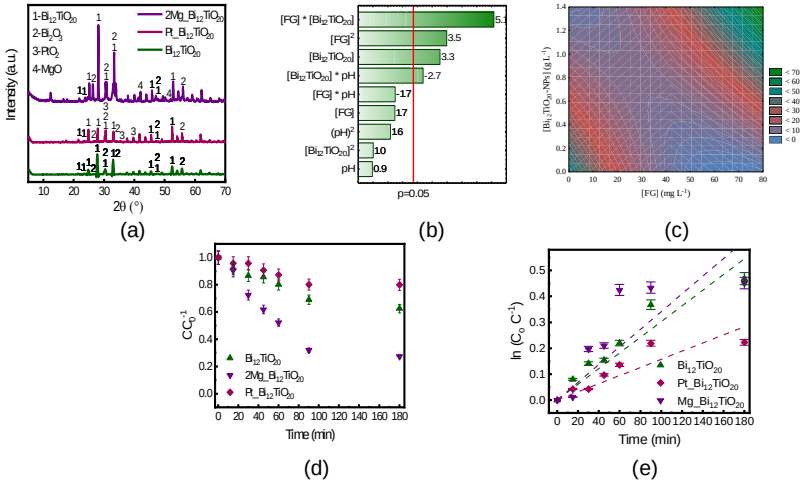

Figure 1. (a) XRD diffractogram; (b) Pareto chart; (c) 2D surface; (d) Photocatalytic activity and (e) kinetic curve in condition ideal.

Conclusions

The $Bi_{12}TiO_{20}$ nanostructure showed FG removal of 37.36 % using the ideal condition of [FG] of 60 mg L^{-1}, [$Bi_{12}TiO_{20}$] of 1 g L^{-1}, and pH at 4 by CCRD 2^3. Pt_$Bi_{12}TiO_{20}$ showed only 20 % removal, representing an insufficient result for removing the organic dye, whereas doping with Mg^{2+} ions showed around 70 % removal for the FG photodegradation. Therefore, presenting a potential application in wastewater treatment correlating sustainability and nanotechnology.

Acknowledgment

Our research group appreciates the financial support provided by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq - PIBIC 19/2022) for assistance and financial support.

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