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PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS USING A COMMERCIAL CATALYST BY HETEROGENEOUS PHOTOCATALYSIS

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ABSTRACT

The continuous growth of the population and industrial has provided an increase in the environmental impact and human health, due to the greater quantities of waste generated, mainly by the presence of organic toxic compounds, such as the dyes. Then, the work aims to evaluate the applicability of heterogeneous photocatalysis in the degradation of the rhodamine B dye, such as a target molecule, using the commercial titanium dioxide catalyst, under ultraviolet and visible radiation. In addition, to study of the effects of the catalyst concentration (5-100 mg L⁻¹), dye concentration (20-100mgL⁻¹) and doping on photocatalytic activity. The catalysts (commercial and doped) were characterized by X-ray diffraction, zeta potential, porosimetry of N₂ and diffuse reflectance spectroscopy. The best condition was 50 mg L⁻¹ for the commercial catalyst and 20 mg L⁻¹ of RhB dye concentration, under UV radiation. In addition, doping with Mg²⁺ provided an increase of about 28 % in photocatalytic activity in relation to non-doped catalyst, as well as changes in structural and textural properties, such as decrease of the band gap energy (E_g), increase in the surface area (SBET), increase in pore diameter (D_p) and volume (V_p) and increase (in module) of the zeta potential (ZP).

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INTRODUCTION

Rapid population and industrial growth have provided a major environmental impact due to the increase in waste generation, coupled with inadequate treatment of waste (CHEN, 2013 and SOON, 2011). In addition, pollution of water resources is mainly caused by the presence of toxic organic and inorganic compounds, which have adverse effects on the environment, aquatic life and human health (SOON, 2011). Moreover, industries that use dyes in their production processes, like as textiles, leather, paper and plastic, consume a large volume of water, generating a significant amount of effluent (RAFATULLAH, 2010). For example, it is estimated that there are more than 100,000 synthetic dyes on the market, with an annual production of more than 700,000 tons worldwide (AL-FAWWAZ, 2016).

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In addition, the fact that many of these compounds are characterized by their toxic nature and mutagenic and carcinogenic properties, thus their presence in waters becomes a threat to public health and the environment (KASSALE, 2015 and SUTEU, 2005). Among these dyes, rhodamine B (RhB) is widely used in the textile industry and as a trace material (BARKA, 2008), potentially harmful to humans, as it can promote cutaneous, ocular and respiratory system irritation (CHENG, 2017). In addition, it is a highly water soluble organic cationic dye belonging to the class of xanthenes, having a molar mass of 479.02 g mol⁻¹ and in its structural formula has chromophoric groups (-C=C-N-), according to Figure 1. Therefore, colored wastewater is one of the problems with regard to its correct treatment, since they significantly affect the photosynthetic activity in aquatic life, reducing the penetration of light, besides being toxic due to the presence of complex aromatic compounds hindering its biodegradation (AKSU, 2005). Thus, several techniques for the degradation and mineralization of these effluents have been investigated,

such as advanced oxidative processes and chemical oxidation (KIST, 2012). Advanced Oxidative Processes (POAs) become an attractive alternative, since they are technologies with a potential to oxidize a large variety of complex organic compounds (MA, 2014), through the action of a highly oxidizing species hydroxyl, (OH^\bullet), capable of reacting with the various resistant organic compounds, mineralizing them in non-toxic forms, such as CO_2 and H_2O (PEREIRA, 2010 and WU, 2016). Moreover, their great advantage is that, during the treatment of the organic compounds, they are destroyed and not only transferred from one phase to another, as in some conventional treatment processes (DEZZOTI, 2003). Among the AOPs, the heterogeneous photocatalysis stands out, which involves oxo-reduction reactions induced by the radiation on the surface of semiconductors (catalysts), such as TiO_2 , CdS, ZnO, WO_3 , ZnS, BiO_3 and Fe_2O_3 (GAYA, 2008). The catalyst most used in heterogeneous photocatalysis is titanium dioxide (TiO_2), in its crystalline anatase phase, because it presents some characteristics, such as: (a) high surface area; (b) high density of superficial active sites; (c) low cost; (d) photostability and chemical stability over a wide pH range; (e) biologically and chemically inert; (f) resistant to physical and chemical corrosion; and water insoluble (CHEN, 2002; KONSTANTINOU, 2004 and LATHASREE, 2004). However, TiO_2 presents band gap energy around 3.2 eV, making it impossible to use it under visible irradiation. In order to increase its photocatalytic efficiency, it is the modification in the surface of the catalyst with metals (doping) (EINAGA, 2004; KOZLOVA, 2006 and YOU, 2005), where these small metal particles facilitate the transfer of TiO_2 photoelectrons, decreasing the recombination between photoelectrons and vacancies and raising quantum yield (SAKTHIVEL, 2004). In this context, the present aims to evaluate the applicability of heterogeneous photocatalysis in the photodegradation of organic pollutants (RhB dye), using the commercial titanium dioxide (TiO_2) catalyst, under ultraviolet and visible radiation. In addition, to study the effect of the reaction parameters, such as organic pollutant concentration, catalyst concentration and doping with magnesium chloride (MgCl_2), in order to determine the best reaction conditions.

MATERIALS AND METHODS

Synthesis of the doped catalyst: For the doping of the commercial catalyst (TiO_2 , Degussa), the impregnation method with the respective photoactive metal precursor (Mg^{+2}) (MgCl_2 , Synth) was used, according the literature (SILVA, 2014). Thus, TiO_2 was mixed with the metal precursor (25% w/w), under continuous magnetic stirring at room temperature for 90 min. Then, the sample was calcined ($450\text{ }^\circ\text{C} / 4\text{ h}$) and uniformized its granulometry.

Characterization of catalysts: The X-ray diffraction technique was used to identify the crystalline phases of the catalysts in an X-ray diffractometer (Bruker Optics, D2 Advance, USA) with a copper tube ($K_{\alpha\text{-Cu}} = 1.5418\text{ \AA}$), in a range of 2θ from 10° to 70° , acceleration voltage and applied current of 30 kV and 30 mA, respectively. Malvern-Zetasizer® model nanoZS (ZEN3600, UK) with capillary cells (DTS 1060) (Malvern, UK) was used to measure the zeta potential (PZ) values of the samples, ie surface charge. The specific surface area, pore diameter and pore volume were determined by porosity of nitrogen (99.99% ultra-white degree, White Martins) in a

Gemini 2375 Micromeritics (Micromeritics Gemini VII 2375 Series, United States) at -196°C . Thus, the samples were pretreated (10^{-2} mbar at $120\text{ }^\circ\text{C}$) for 24 hours, and the specific area (S_{BET}) was determined by the Brunauer-Emmett-Teller equation (BET) in the range of $P/P_0 = 0.05$ to 0.35 . The porosity was calculated using the Barrrt-Joyner-Halenda equation (BJH). Band gap energy was determined by diffuse reflectance spectroscopy (DRS) on a UV-Vis spectrophotometer (Cary 100 Scan, UV-Vis Spectrophotometers, United States) with DRA-CA-301 accessory (Labsphere, United States) coupled for analysis in diffuse reflectance mode.

Photocatalytic activity: For the evaluation of the photocatalytic activity, a jacketed batch reactor was used with slurry catalysts, as adapted from the literature (SILVA, 2014). Thus, for the effect of the catalyst loading, 50 mL of the solution containing the target molecule (20 mg L^{-1}) were added at different concentrations of the commercial catalyst (5 mg L^{-1} - 100 mg L^{-1}). Then, for the study of the effect of the initial concentration of RhB, the concentration of the catalyst determined in the first study was used, varying the concentration of the target molecule (20 - 100 mg L^{-1}). It should be noted that the study of the best conditions was carried out under ultraviolet radiation and the evaluation of the effect of the doping on the photocatalytic activity of the commercial TiO_2 under visible radiation, after determination of the best conditions. All the photocatalytic test were carried out in two stages, where: (a) the first stage performed in the absence of radiation, where the adsorption / desorption equilibrium of the target molecule on the catalyst surface during 60 min and (b) the second stage with presence of radiation (UV or visible). The degradation monitoring was carried out by means of sampling, with collected at predetermined times (0, 5, 15, 30, 45, 60, 75, 90 and 120 min). Then, the samples were centrifuged (refrigerated digital bench centrifuge, Cientec CT-5000R, Brazil) for 20 min with a rotation of 5,000 rpm, at $25\text{ }^\circ\text{C}$ and 1 min of acceleration/deceleration. After, the samples were diluted (0.5 mL of the sample in 5 mL of distilled water) in an amber glass vial. For the advancement of the reaction, absorbance measurements of the solutions collected during the reaction were performed and read on a double beam spectrophotometer (Varian, Cary 100, United States), at the 553 nm wavelength characteristic of rhodamine B. All photocatalytic tests were carried out in duplicate (with error less than 5%) and the radiation adjusted to 61.8 W m^{-2} for ultraviolet (Radiometer Cole-Parmer Instrument, Radiometer Series 9811, USA) and 202 W m^{-2} (Piranometer SL100, Kimo® Instruments, United States).

Photodegradation kinetics: Kinetics interpretations were conducted as a function of the remaining concentration of phenol in solution over time. Data were fitted as kinetic model of Langmuir-Hinshelwood (L-M) (KONSTANTINOU, 2004 and HERRMANN, 2005), according to equation (1):

$$-r_i = -\frac{dC_i}{dt} = \frac{\kappa_s \cdot K \cdot C_i}{1 + K \cdot C_i} \dots\dots\dots(1)$$

where κ_s is the true photodegradation rate of the organic compound, C_i the concentration of the compound, t the illumination time, and K the adsorption coefficient of the compound to be degraded. κ_s is related to several parameters such as mass of catalyst, efficient photon flow and layer of

oxygen. The L-H model can be simplified to a pseudo-first-order kinetic equation and k is the apparent rate of the pseudo-first-order reaction, according to equations (2) and (3) (Konstantinou, 2004).

$$-r_i = -\frac{dC_i}{dt} = \kappa_s \cdot K \cdot C_i \quad \dots\dots\dots(2)$$

$$\ln\left(\frac{C_{i0}}{C_i}\right) = \kappa_s \cdot K \cdot t = \kappa \cdot t \text{ or } C_i = C_{i0} \cdot e^{-\kappa t} \quad \dots\dots\dots(3)$$

Pseudo first-order reaction rate constant was determined from the slope of the linear regression of $\ln(C_0/C_i)$ versus time.

RESULTS AND DISCUSSION

Characterization of the catalysts: Table 1 shows the results of the characterization of the commercial catalyst (TiO_2) and the doped catalyst (Mg-TiO_2).

Table 1. Results of the surface area (S_{BET}), pore diameter (D_p), pore volume (V_p), band gap energy (E_g), wavelength (λ) and zeta potential (ZP) of the catalyst commercial and doped with Mg^{+2}

Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	D_p (nm)	V_p ($\text{cm}^3 \text{g}^{-1}$)	λ (nm)	E_g (eV)	ZP (mV)
TiO_2	56	4.8	0.07	371.2	3.3	-24.0
Mg-TiO_2	382	16.8	0.09	720.9	1.7	-22.3

According to Table 1, the doping with Mg^{+2} carried out changes in the structural and textural properties of the commercial catalyst (TiO_2), such as an increase from 56 to 382 $\text{m}^2 \text{g}^{-1}$ in the specific area, from 4.8 to 16.8 nm in the pore diameter and 0.07 to 0.09 $\text{cm}^3 \text{g}^{-1}$ in the pore volume. In addition, a reduction of the band gap energy from 3.3 to 1.7 eV and an increase (in module) in the zeta potential from -24 to -22.3 mV. Therefore, for heterogeneous photocatalysis, the ideal is that the catalyst has a high specific area to promote more adsorption of the pollutant to be degraded, as well as a significantly large porosity to promote diffusion of the pollutant to the catalytic surface of the photocatalyst (WANG, 2018). Moreover, the effect of the dopant metal promoted a reduction on E_g , causing a shift towards light absorption in the visible range and thus directly affecting the photocatalytic activity (BAVYKIN, 2006). This was possibly due to the fact that, with magnesium doping (Mg^{+2}), the concentration of the electron acceptor / donor species (e_{BC}^- and h_{BV}^+) increases, followed by a decrease in polarization of the O_2^- ion in the conduction band.

Thus, it promotes a change in the conduction bands and the valence band levels, promoting a reduction in the energy band range of the catalysts (VADIVEL, 2015). In addition, the RhB molecule characterized by a positive charge, due to its cationic nature (DEBRASSI, 2011 and SALLEH, 2011), and the catalysts have a negative charge, then RhB dye tends to adsorb on the catalytic surface of the catalysts by means of the attractive forces, thus allowing the pollutant degradation. Moreover, through the pore diameter can be affirmed that they are structures with mesopores (IUPAC, 1972). Figure 2 shows the diffractogram of the Mg-TiO_2 catalyst indicating the presence of peaks characteristic of the crystalline phase MgO periclase (43.5° and 47.2°), indicating that the doping was

successfully performed. In addition, according to JCPDS (Joint Committee for Powder Diffraction Standards - n° 21-1272 Anatase TiO_2), characteristic peaks of the anatase photoactive phase were identified at 25.23° , 37.72° and 62.51° .

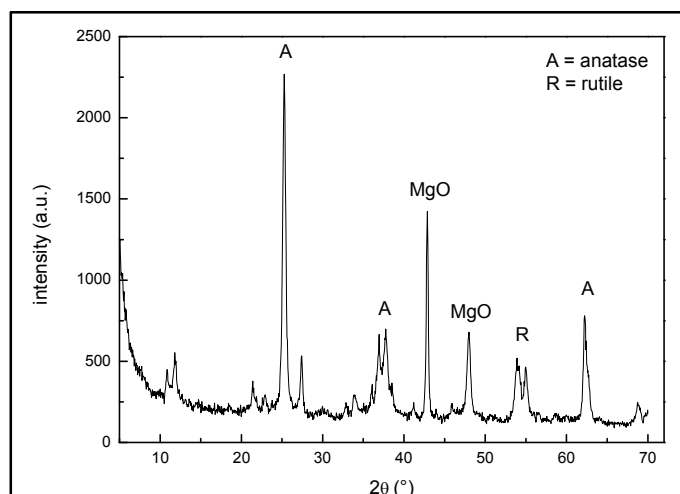


Figure 2. Diffractogram of the doped catalyst (Mg-TiO_2), indicating the presence of the anatase and rutile phases of TiO_2 , and the dopant metal Mg^{+2}

Effect of catalyst concentration: The increase in catalyst concentration promotes an increase in the rate of degradation of the organic contaminants, up to a limit value. Thus, this limit is caused essentially by two factors: (i) aggregation of the catalyst particles at high concentrations, leading to a decrease in the number of active sites on the surface, and (ii) increase in the opacity of the reaction medium, causing a reduction of irradiation passage through the reactor (CARP, 2004). Thus, in order to determine the effect of the catalyst concentration on the photocatalytic degradation of rhodamine B, tests were performed by varying the amount of TiO_2 from 5 mg L^{-1} to 100 mg L^{-1} under UV radiation and an initial concentration of dye of 20 mg L^{-1} . Figure 3 shows the degradation rate versus the commercial catalyst concentration, as well as the specific rate (k) for each concentration evaluated. According to the Figure 4, it was possible to verify that the degradation rate followed a kinetics of the order of the pseudo-first order and the best evaluated concentration of catalyst obtained was 50 mg L^{-1} ($48.2\% \text{ e } k = 0.0053 \text{ min}^{-1}$), after 120 minutes of reaction under UV radiation. In addition, a degradation of 12.1% ($k = 0.0011 \text{ min}^{-1}$), 29.2% ($k = 0.027 \text{ min}^{-1}$) and 37.9% ($k = 0.0038 \text{ min}^{-1}$) was obtained for the concentrations of 5, 25 and 100 mg L^{-1} respectively. Thus, for the next photocatalytic tests, this best concentration was used.

Effect of the initial concentration of the RhB dye: The initial concentration of the RhB dye is another parameter of great importance to be verified in the photocatalytic process, since decreasing the initial concentration of the pollutant causes an increase in the rate of degradation of the reaction, due to the higher number of molecules of water are adsorbed by the photocatalyst, generating hydroxyl radicals that aid in the degradation of the dye, increasing the specific speed of the reaction [33]. Thus, the degradation rate of the RhB dye was determined in an initial concentration range of 20 mg L^{-1} - 100 mg L^{-1} , maintaining the determined best TiO_2 concentration (50 mg L^{-1}), under UV radiation. Figure 4 shows the degradation rate versus the initial concentration of RhB dye and the specific rate (k) for each concentration studied.

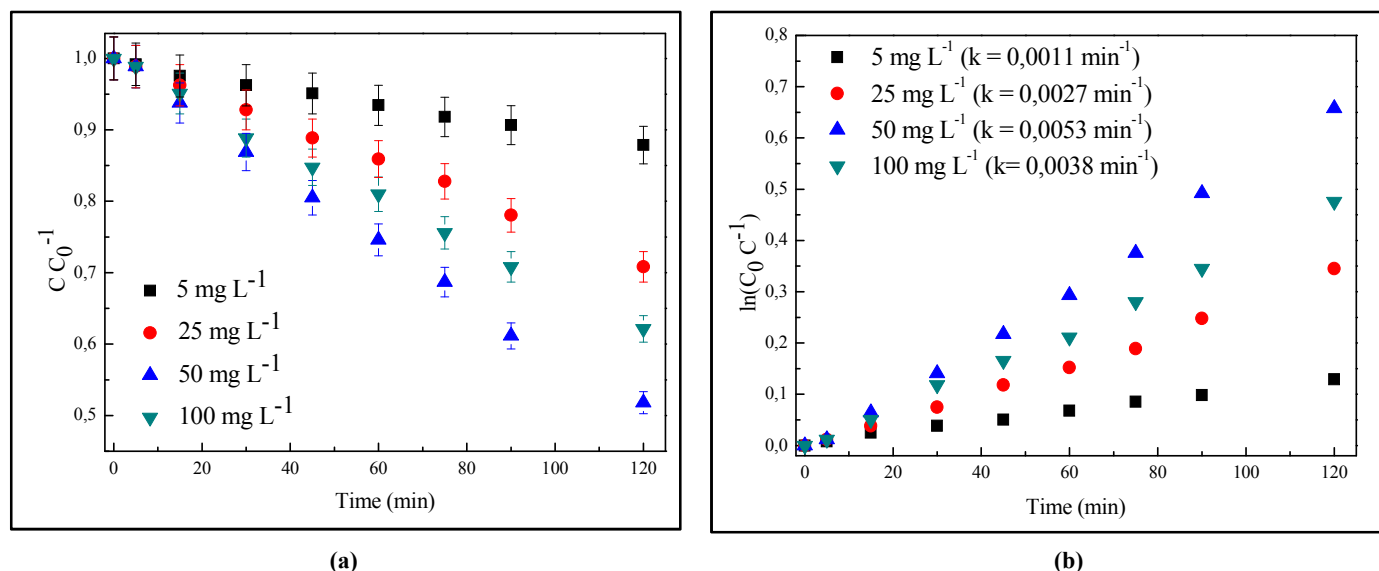


Figure 3. (a) The effect of commercial TiO_2 concentration on RhB dye photodegradation at 120 min irradiation time, and (b) the pseudo-first order rate constant versus catalyst concentration ($C_{\text{TiO}_2} = 5\text{-}100 \text{ mg L}^{-1}$, $C_{\text{RhB}} = 20 \text{ mg L}^{-1}$, $T = 25 \pm 2^\circ \text{ C}$, natural pH and UV radiation intensity of 61.8 W m^{-2})

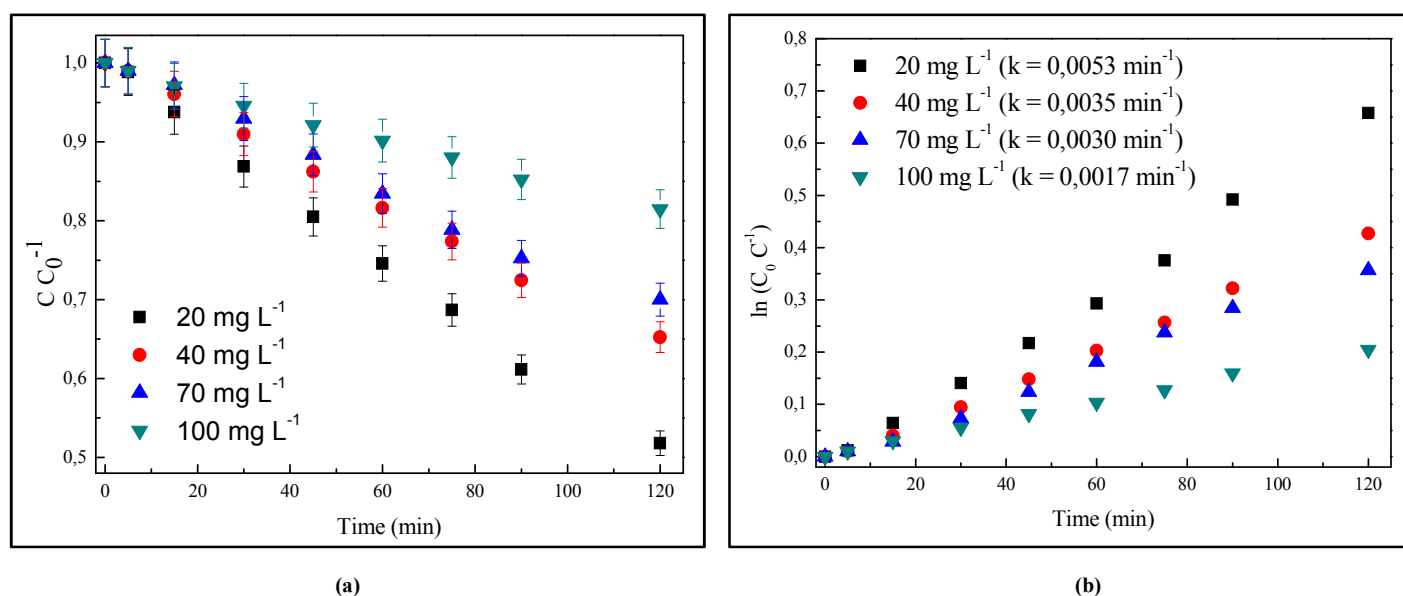


Figure 4. (a) The effect of the initial concentration of the RhB dye using the commercial catalyst TiO_2 at 120 min irradiation time, and (b) the pseudo-first order rate constant versus the initial concentration of RhB ($C_{\text{TiO}_2} = 50 \text{ mg L}^{-1}$, $C_{\text{RhB}} = 20\text{-}100 \text{ mg L}^{-1}$, $T = 25 \pm 2^\circ \text{ C}$, natural pH and UV radiation intensity of 61.8 W m^{-2})

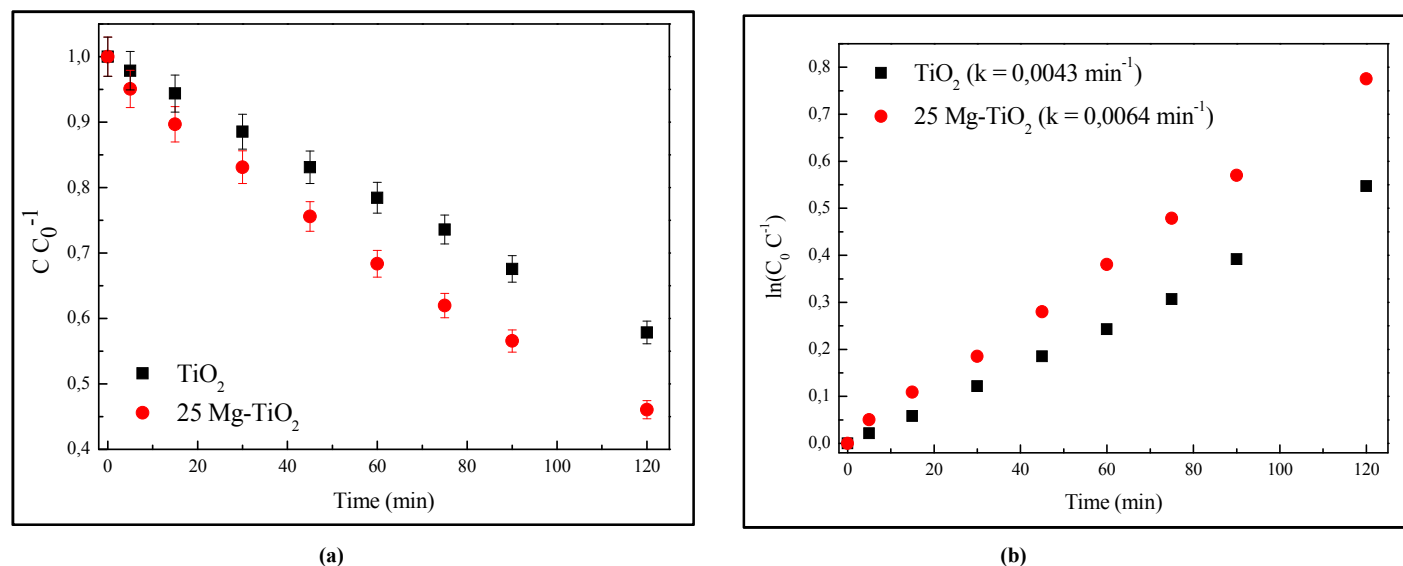


Figure 5. (a) Effect of doping with Mg^{2+} on the photocatalytic activity and (b) the specific rate constant of the RhB dye degradation reaction under visible radiation after 120 minutes of reaction ($C_{\text{cat}} = 50 \text{ mg L}^{-1}$, $C_{\text{RhB}} = 20 \text{ mg L}^{-1}$, $T = 25^\circ \text{ C}$, natural pH and visible radiation intensity of 202 W m^{-2})

According to the Figure 4, it was possible to verify that the best evaluated concentration of the target molecule (RhB) was 20 mg L⁻¹ (48.2% and $k = 0.0053 \text{ min}^{-1}$), following a pseudo first order model after 120 minutes of reaction under UV radiation. In addition, to the 40, 70 and 100 mg L⁻¹ concentrations of RhB were obtained a degradation of 34.8% ($k = 0.035 \text{ min}^{-1}$), 30% ($k = 0.003 \text{ min}^{-1}$) and 18.5% ($k = 0.002 \text{ min}^{-1}$), respectively.

Effect of doping: The doping with metallic ions has a great influence on the photocatalytic activity in the photocatalysts, since the incorporation of these in the crystalline matrix introduces band gap levels near the valence band, allowing a displacement to the visible region and its application under solar radiation (NOWOTNY, 2008). The effect of doping with magnesium (Mg⁺²) on the photocatalytic activity under visible radiation was evaluated after the determination of the best conditions of the photocatalyst concentration and the initial concentration of RhB dye, according to Figure 5. According to the Figure 5, it was possible to verify the positive effect of doping with Mg⁺², since it provided an increase of about 28% in the photocatalytic activity, where it promoted a degradation of 53.9% after 120 minutes of reaction under visible radiation, while the non-doped catalyst presented 42.1%, for the same reaction conditions. This increase in activity is associated with the structural and structural changes that the Mg⁺² promoted in the commercial catalyst, such as increase in specific area (S_{BET}), increase in porosity (Dp and Vp), reduction of energy Eg and increase zeta potential. It is noteworthy that all the photocatalytic tests were performed for the best conditions already determined, ie the catalyst concentration of 50 mg L⁻¹, RhB concentration of 20 mg L⁻¹, operating temperature of 25 °C, natural pH of the dye (≈ 4.3) and radiation intensity of 202 W m⁻².

Conclusions

According to the characterization and photocatalytic activity results, it can be concluded that the photodegradation kinetics of the rhodamine B dye can be approximated to a pseudo-first order model and that the doping with MgCl₂ (Mg⁺²) provided changes in the textural properties and structural changes in relation to the non-doped catalyst, such as band gap energy (Eg), increase of about 6 times in surface area (S_{BET}), increase of 2.5 times in pore diameter (Dp), increase in pore volume (Vp), increase (in modulus) of the surface charge (PZ) and a better photocatalytic performance in the degradation of RhB dye, on the visible radiation. Thus, these results suggest that the positive effect of magnesium as a dopant on the development of catalysts, due to the fact that Mg⁺² is capable of generating an intermediate band gap energy between conduction and valence bands of the non-doped sample, capable of promote the absorption of photons and generate more electron pairs/vacancies (e_{BC}⁻ and h_{BV}⁺) and thus provide a higher formation of the hydroxyl radical (·OH). Therefore, the best reaction conditions obtained were 50 mg L⁻¹ of catalyst and 20 mg L⁻¹ of initial concentration of RhB dye.

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