

REMOVAL OF DIRECT BLACK 38 DYE BY ADSORPTION AND PHOTOCATALYTIC DEGRADATION ON TiO₂ PREPARED AT LOW TEMPERATURE

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Abstract— TiO₂ powder was prepared by a hydrothermal process at 200°C for 12 h. The material was characterized by X-ray diffraction and N₂ adsorption-desorption isotherm. The synthesized sample presented a pure phase anatase, with nanometric particle size. Its activity was tested for adsorption and degradation of the azo leather dye, Direct Black 38. The adsorption isotherm obtained followed the S-type in terms of the classification of Giles. Thermodynamic parameters were calculated, and the results revealed that the adsorption process is endothermic in nature. The material showed highly photocatalytic activity in the degradation of the dye, similar to that of the TiO₂ (P25 Degussa) photocatalyst.

Keywords— TiO₂, photocatalysis, adsorption, degradation, dye.

I. INTRODUCTION

Dye effluents may lead to certain environmental problems. Effluent treatment for dye-containing effluents from tanneries and textile and paper industries is currently capable of removing only about half of the dyes lost in residual liquors (Moreira *et al.*, 2005). Advanced oxidation processes (AOPs) have been proposed as an alternative method for water purification and an efficient wastewater treatment technique used for the total mineralization of organics (Akyol *et al.*, 2004). AOPs include ozonation, UV irradiation, photocatalysis, the Fenton and photo-Fenton reagent, and various combinations of these (Tarek *et al.*, 2009).

The photocatalytic degradation of toxic compounds in aqueous media provides a new method for wastewater treatment. The process couples low-energy ultraviolet light with semiconductors acting as photocatalysts. TiO₂ is generally used as a photocatalyst for the removal of organic pollutants (Tanaka *et al.*, 1997) and dye pollutants (So *et al.*, 2002) due to its high photocatalytic activity and stability, low cost, stability with respect to corrosion, and biological, nontoxic and chemical inertness (Ferguson *et al.*, 2005).

Different methods have been employed for the synthesis of titanium dioxide, as follow: chemical precipitation (Scolan and Sanchez, 1998), sol-gel method (Lin *et al.*, 2006a), hydrothermal (Wu *et al.*, 2002) and solvothermal processes (Yin *et al.*, 2003). Hydrothermal synthesis has become one of the notable methods employed in nano-material production and nanotechnology (Pavasupree *et al.*, 2008). The process includes a simple

route and produces high crystallinity oxides under moderate conditions: low temperatures and short reaction times. It is one the most used methods to produce ceramic materials as it allows the control of particle size, morphology (Lin *et al.*, 2006a) and phase composition (Wang *et al.*, 2007).

In this study, TiO₂ was synthesized by the hydrothermal method at 200°C for 12 h. Its characterization, adsorption capacity and photocatalytic activity in the degradation of azo leather dye, Direct Black 38, was investigated. Various thermodynamic parameters, such as entropy (ΔS°), heat of adsorption (ΔH°) and Gibbs free energy (ΔG°) have been determined.

II. METHODS

A. Catalyst preparation

The synthesis of titanium dioxide was performed using hydrothermal treatment. The molar composition of the reaction mixture was 1TiO₂:10CH₃COOH:150H₂O. Both glacial acetic acid (CH₃COOH) (Aldrich) and titanium (IV) isopropoxide (C₁₂H₂₈O₄Ti) (Aldrich) were of analytical-reagent grade and used as starting materials. Glacial acetic acid (36 mL) was slowly added to 20 mL of titanium (IV) isopropoxide in a water bath at 0°C, under constant stirring. Afterwards, deionized water (170 mL) was gently added to the mixture under constant stirring. The solution was then mixed together under vigorous agitation for one hour and subsequently underwent ultrasonic treatment for 30 min. Once again, vigorous agitation was applied for 5 h. Afterwards, the solution was poured into teflon jars and placed in stainless steel autoclaves. The autoclaves were placed in an oven previously heated to 70°C in order to carry out the ageing process for 12 h. Following the ageing process, hydrothermal treatment was carried out 200°C for 12 h. Subsequently, the autoclaves were removed from the oven and cooled in running water. Eventually, the precipitate was washed with distilled water, centrifuged and dried in an oven at 100°C for 12 h. The solid sample obtained was finely ground using a mortar and pestle and stored in plastic containers.

B. Characterization methods

The powder was characterized by X-ray diffraction and nitrogen adsorption was determined by BET. X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance diffractometer with a Cu-K α radiation X-ray source (40 kV e 40 mA). Data were collected over the 2 θ range 20–80° with a step size of 0.05° and a count time of 35 s. The average nanocrystal size was estimat-

ed using the Sherrer equation. The Brunauer-Emmett-Teller (BET) surface area measurements were carried out by N₂ adsorption-desorption at 77 K using a Quantachrome Autosorb Automated Gas Sorption instrument, in the relative pressure range (P/P₀) of 0 to 0.99.

C. Adsorption Study

For the adsorption tests, 0.2 g of TiO₂ was added to 200 mL of the aqueous solution of azodye Direct Black 38 (DB38) at different initial concentrations and at optimum pH 2.5, which was adjusted by using dilute H₂SO₄. The pH 2.5 was determined by previous studies conducted by Moreira *et al.* (2005) as the optimal value. The resulting solution was stirred continuously using a magnetic stirrer (100 rpm) at a constant temperature of 25°C to achieve the adsorption equilibrium of dye on the catalyst. An aliquot of the aqueous solution was taken at various time intervals, centrifuged and filtered through a PVDF membrane (0.22 μm) before analysis. The concentration of dye in aqueous solution was determined by spectrometry (Spectro vision model T6-UV) at λ_{max} 590 nm. UV-vis adsorption spectrum of DB38 aqueous solution at pH 2.5 was shown in a previous study (Moreira *et al.*, 2005).

D. Photocatalysis Study

The photocatalytic activity of the commercially available TiO₂ Degussa P25 was also evaluated and compared with that of TiO₂. TiO₂ Degussa P25 is mostly in the anatase form (80% anatase form and 20% rutile) and has a BET surface area of 50 m².g⁻¹ corresponding to a mean particle size of 30 nm, and mean pore diameter of about 6.9 nm.

The reactor was batch-type, consisting of a glass tube (internal diameter of 7.5 cm and 18.0 cm in height) with a mercury vapor lamp (80 W) fixed at the center and protected by a bulb of quartz. The outside of the reactor was covered with aluminum foil to protect from external UV radiation, so that the rays were reflected into the reactor. Furthermore, the reactor was equipped with an aluminum cylinder to keep the temperature constant. The photocatalytic degradation of dye DB38 was studied for different initial concentrations of dye and different concentrations of catalyst, at pH 2.5, 25°C and a fixed volume of 400 mL of solution. Prior to photoirradiation, the suspensions underwent ultrasound for 10 min. Before illumination, the suspension with DB38 and photocatalyst was magnetically stirred for 60 min to establish the adsorption equilibrium. An initial sample was taken out for analysis at the end of the adsorption period, in order to determine the bulk concentration. This was considered as the initial concentration (hereafter denoted C₀) for the photocatalytic experiment from which the rate constants were determined.

The mercury vapor lamp was turned on and the solution was stirred (100 rpm) using a magnetic stirrer and aliquots were taken at certain periods of time. These samples were centrifuged and filtered with a PVDF membrane (0.22 nm) before the analysis of color. The degradation of the dye was monitored by measuring the

absorbance at 590 nm until the process reached the equilibrium.

III. RESULTS AND DISCUSSION

A. Characterization of TiO₂

Figure 1 (a) shows XRD for the TiO₂ sample synthesized. The diffractogram shows the complete formation of the crystalline anatase phase, indexed according to JCPDS card No. 89-4921. The Fig. 1 (b) shows the isotherm adsorption/desorption of nitrogen for the titanium dioxide synthesized. The curve shows a type IV isotherm and its hysteresis loops, typical of mesoporous materials according to the recommendations of IUPAC (International Union of Pure and Applied Chemistry). The crystalline size, surface area, and total pore volume of the resulting sample were 13 nm, 113 m².g⁻¹ and 0.31cm³.g⁻¹, respectively.

B. Considerations on adsorption

Figure 2 shows the kinetics of dye adsorption on TiO₂ at different initial dye concentrations. The experimental conditions were: C_{catalyst} = 1 g.L⁻¹, pH = 2.5, temperature = 25°C. Observe that for all concentrations, the equilibrium is reached in the first 10 min. This is due to the fact that the material synthesized has a high surface area, thus providing many sites available for adsorption, resulting in an increase in the concentration gradient of adsorbate to adsorbent surface. This increase in the dye concentration gradient tends to increase the adsorption of the dye in the initial stage.

The analysis of the adsorption process requires a study of adsorption equilibrium. The adsorption equilibrium test provides physico-chemical data for the appli-

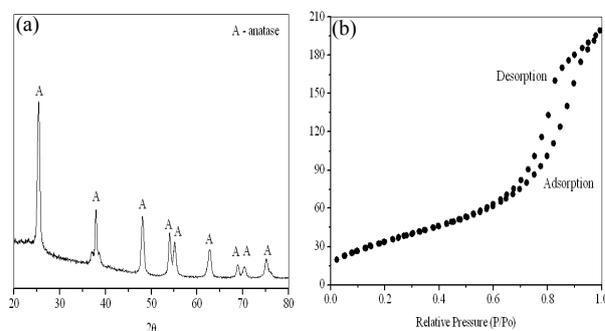


Fig. 1. (a) XRD of the TiO₂ sample synthesized and (b) N₂ adsorption-desorption isotherm.

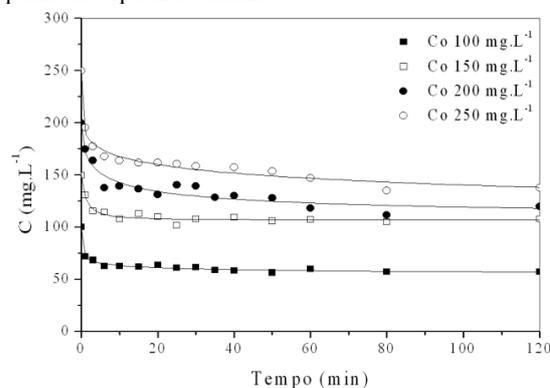


Fig. 2: Kinetic of adsorption of DB38 on TiO₂ with different initial dye concentrations.

cability of adsorption. The two most commonly used equilibrium relations are Freundlich and Langmuir isotherm equations. The equation describing the Langmuir isotherm is given by (Vadivelan and Kumar, 2005):

$$qe = \frac{qo \times K_L \times Ce}{1 + K_L \times Ce} \quad (1)$$

where qo is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface (mg.g^{-1}), K_L is the Langmuir constant related to the energy of adsorption (L.mg^{-1}). The Langmuir constants qo and K_L were calculated from the slope of the plot between $1/qe$ versus $1/Ce$ (not shown). Through this plot $1/qe$ versus $1/Ce$, the values of these parameters to fit the experimental data were qo of 122 mg.g^{-1} , K_L of 0.019 L.mg^{-1} and with a correlation coefficient (r^2) of 0.69. Through the low value of r^2 note that the inability of the Langmuir model to represent the experimental data could have been due to the fact that this isotherm does not take adsorbate-adsorbate interactions into account. The equation that describes the Freundlich isotherm is given by (Gómez *et al.*, 2007):

$$qe = K_F \times Ce^{(1/n)} \quad (2)$$

where K_F is the adsorption capacity (mg.g^{-1}) and $1/n$ is the adsorption intensity (L.g^{-1}).

Through the plot $\log qe$ versus $\log Ce$ (not shown), the values of these parameters to fit the experimental data were K_F 1.28 mg.g^{-1} , $1/n$ of 1.15 L.g^{-1} with a correlation coefficient (r^2) of 0.87. The Freundlich equation provided a more satisfactory description when compared to the Langmuir isotherm.

Using the Giles classification (Giles *et al.*, 1997), the experimental isotherm obtained in present study was the S-type (Fig. 3). The initial part of the S curve indicates few interactions between dye and the solid at low concentrations. However, as the concentration in the liquid phase increased, adsorption occurred more readily. This behavior is due to a synergistic effect, with the adsorbed molecules facilitating the adsorption of additional molecules as a result of attractive adsorbate-adsorbate interactions. Gómez *et al.* (2007) and Gürses *et al.* (2006) found S-type isotherms for adsorption of various dyes on activated carbon.

The study of thermodynamics of adsorption was carried out at a temperature ranging from 25 to 55°C in order to determine ΔG° , ΔH° and ΔS° . The Gibbs free energy of the adsorption process is related to the equilibrium constant by the classical Van't Hoff equation (Uma *et al.*, 2009).

$$\Delta G^\circ = -RT \ln K_D \quad (3)$$

The Gibbs free energy change is also related to the entropy change and heat of adsorption at constant temperature according to the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

Combining the above equations:

$$\ln K_D = -\frac{\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \times \frac{1}{T} \quad (5)$$

where ΔG° is the free energy change (J.mol^{-1}), ΔH° the change in enthalpy (J.mol^{-1}), ΔS° the entropy change

Table 1: Thermodynamics parameters of the adsorption of dye on titanium dioxide ($C_o=200\text{mg.L}^{-1}$, $C_{adsoben}=1 \text{ g.L}^{-1}$, $\text{pH}=2.5$)

T (K)	K_D (L.g^{-1})	ΔG° (J.mol^{-1})	ΔH° (J.mol^{-1})	ΔS° ($\text{J.mol}^{-1}.\text{K}^{-1}$)
298	0.476	832	560	16
308	0.840	672		
318	0.871	512		
328	0.918	352		

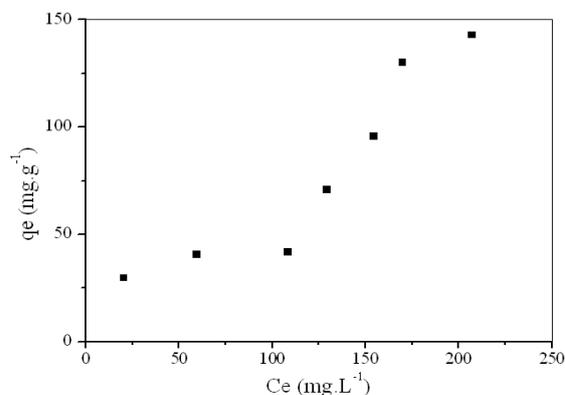


Fig. 3: Isotherm of DB38 adsorption on TiO_2 .

($\text{J.mol}^{-1}.\text{K}^{-1}$), T is the absolute temperature (K), R is the universal gas constant ($8.314 \times 10^{-3} \text{ KJ.mol}^{-1}.\text{K}^{-1}$) and K_D (qe/Ce) is the single point or linear adsorption distribution coefficient.

The ΔH° can be determined by the slope of Van't Hoff equation, $\ln K_D$ versus $1/T$ using the equation:

$$\Delta H^\circ = \left[R \times \frac{d \ln K_D}{d(1/T)} \right] \quad (6)$$

Table 1 shows the values found for the thermodynamics parameters. The positive value for enthalpy change means that the adsorption of this compound is endothermic, i.e., the removal of dye is favored by increasing temperature. As the value obtained for enthalpy was 560 J.mol^{-1} , or that is, less than $40.000 \text{ J.mol}^{-1}$ (Sankar *et al.*, 1999) with weak forces of Van der Waals (Wedler, 1976) has been the characterization of a physical nature of adsorption. The positive value of ΔS° suggest increased randomness at the solid/solution interface with the increased of temperature. As for the variation of Gibbs free energy, positive values indicate that the enthalpic contribution is higher than the entropic contribution. It is observed that the variation of Gibbs free energy decreases with increasing temperature, showing that the adsorption is more favorable at higher temperatures.

C. Considerations on photocatalysis

The degradation of DB38 has been investigated to determine whether degradation occurred when the dye solution was irradiated with UV in the presence of TiO_2 (P25-Degussa) and TiO_2 synthesized by hydrothermal suspension. Figure 4 shows the photocatalytic degradation of DB38 as a function of irradiation time for both photocatalysts. The photoactivity of TiO_2 was similar to that of TiO_2 -P25, which may be attributed to its great specific surface area ($113 \text{ m}^2.\text{g}^{-1}$), high crystallinity and nanometric particle size (13 nm). It is interesting to note

that TiO₂ and P25 exhibit similar activity despite have different properties such as crystalline phase composition, particle size and BET area. The P25 powder is manufactured by the Aerosil process, by which titanium tetrachloride is subjected to hydrolysis in vapor phase at an elevated temperature (Bickley *et al.*, 1991). Different preparation methods have been employed for the two samples and this could affect properties such as active site density, aggregate particle size in solution and other nano-structural parameters and consequently alter reactivity (Gumy *et al.*, 2006). The anatase phase of TiO₂ is considered the more active (Linsebigler *et al.*, 1995), however, the mixed structure of 80/20 anatase/rutile (P25) may cause a synergy effect which must be the key to the high activity of the P25 (Ohno *et al.*, 2001).

The effect of initial DB38 concentration on the rate of degradation was investigated, varying the concentration from 25 to 95 mg.L⁻¹, and leaving the concentration of TiO₂ constant at 1.0 g.L⁻¹. Figure 5 shows the effect of the initial dye concentration on the photocatalytic degradation of DB38 and the influence of photolysis on the degradation process. As seen in Fig. 5, there is a negligible influence of photolysis on the degradation of the dye. Note that by increasing the concentration of dye, the rate of degradation decreases. Similar results have been presented for the degradation of other dyes (Wang, 2007). Ishiki *et al.* (2005) reported that this can be justified by the number of active sites at the TiO₂/H₂O interface. Thus, at a lower concentration of dye, there are many more water molecules that will be adsorbed on the available TiO₂ particles, producing hydroxyl radicals and leading to a rapid oxidation process. In contrast, at higher concentrations of dye there is a smaller proportion of adsorbed water molecules on the catalyst surface because the number of available active sites remains the same. Consequently, competitive adsorption between the dye and water molecules increases and leads to a decrease of the rate constant. The other possible cause is the interference of intermediates formed upon the degradation of dye (So *et al.*, 2002).

The initial degradation rate of most organic pollutants is described by the Langmuir Hinshelwood (L-H) model, which is accepted by a great number of re-

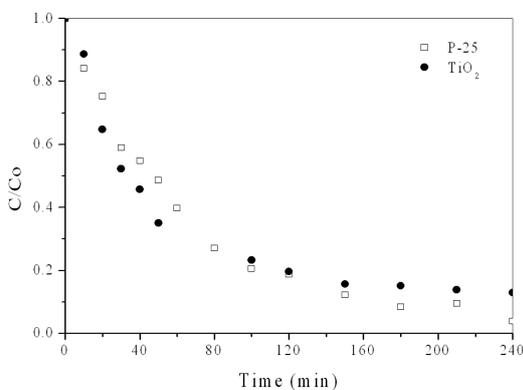


Fig. 4: Photocatalytic degradation of DB38 as a function of time irradiation. Experimental conditions: $C_o = 100 \text{ mg.L}^{-1}$, $C_{catalyst} = 1 \text{ g.L}^{-1}$, $\text{pH} = 2.5$, $T = 25^\circ\text{C}$.

Table 2: Values of k_{app} and corresponding r_o

Co (mg.L ⁻¹)	k_{app} (min ⁻¹)	r_o (mg.L ⁻¹ .min ⁻¹)	r^2
25	0.09	2.45	0.98
55	0.04	2.22	0.98
80	0.02	1.79	0.98
95	0.01	1.06	0.99

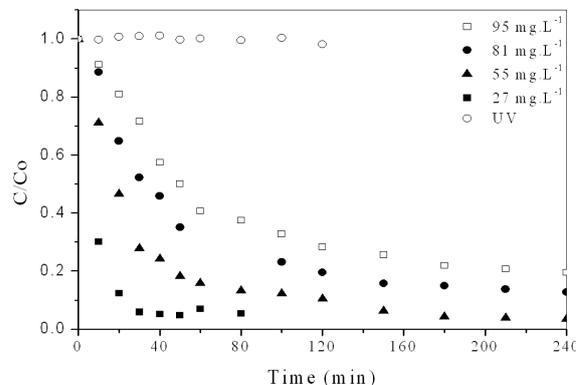


Fig. 5: Effect of initial concentration on the photocatalytic degradation of DB38 for different initial dye concentrations. Experimental conditions: $C_{catalyst} = 1 \text{ g.L}^{-1}$, $\text{pH} = 2.5$, $T = 25^\circ\text{C}$

searchers (Konstantinou and Albanis, 2004). It basically relates the degradation rate (r) and reactant concentration in water (C) at time t , which is expressed as follows:

$$r = -\frac{dC}{dt} = \frac{k_r \cdot K_{LH} \cdot C}{1 + K_{LH} \cdot C} \quad (7)$$

where r is the degradation rate of the reactant (mg L⁻¹.min⁻¹), C the concentration of the reactant (mg. L⁻¹), t the illumination time (min), k_r the constant of reaction rate (mg.L⁻¹.min⁻¹), K_{LH} the adsorption equilibrium constant of the reactant (L.mg⁻¹). When the adsorption is relatively weak and/or the reactant concentration is low, Eq. (7) can be simplified to the pseudo-first-order kinetics with an apparent first-order rate constant (k_{app}):

$$\ln\left(\frac{C_o}{C}\right) = k_r \cdot K_{LH} \cdot t = k_{app} \cdot t \quad (8)$$

where C_o is the initial concentration (mg.L⁻¹), k_{app} is the apparent constant rate of degradation (min⁻¹) and $k_r \cdot K_{LH} = k_{app}$. The initial degradation rate could be then deduced from Eq. (9):

$$r_o = k_{app} \cdot C_o \quad (9)$$

The plot $\ln(C_o/C)$ versus time in Fig. 6 represents a straight line. The slope of linear regression is equal to the apparent first-order constant k_{app} . Their values corresponding to different initial concentrations are in Table 2. The observed decrease in k_{app} as the initial concentration of dye increases is explained by the lower availability of photons as the color of the solution gets deeper. The presumed reason is that at high dye concentrations the generation of $\cdot\text{OH}$ radical on the surface of the catalyst is reduced since the active sites are covered by dye ions (Konstantinou and Albanis, 2004). At a high dye concentration, a significant amount of UV may be absorbed by the dye molecules rather than the TiO₂ particles, which reduces the efficiency of the catalytic

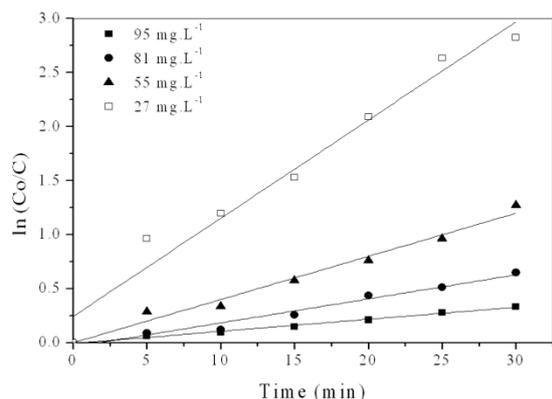


Fig. 6: Plot of $\ln(Co/C)$ as a function of time irradiation. Experimental conditions: $C_{catalyst} = 1 \text{ g.L}^{-1}$, $\text{pH} = 2.5$, $T = 25^\circ\text{C}$.

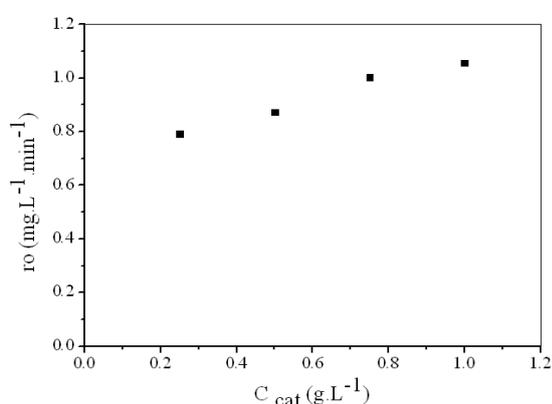


Fig. 7: Dependence of initial rate of DB38 degradation on catalyst loading in slurry TiO_2 system.

reaction because the concentrations of $\cdot\text{OH}$ decrease (So *et al.*, 2002).

The linear form of the Langmuir-Hinshelwood model, in the following expression, translates the dependence of Co/ro values for the respective Co values of dye concentration.

$$\frac{C_o}{r_o} = \frac{1}{k_r \cdot K_{LH}} + \frac{1}{k_r} \cdot C_o \quad (10)$$

Through the plot Co/ro versus Co (not shown), the values of k_r and K_{LH} are determined. The k_r and K_{LH} values calculated from the slope of the straight line ($r^2 = 0.97$) and from the ordinate were $0.953 \text{ mg.L}^{-1}.\text{min}^{-1}$ and 0.042 L.mg^{-1} , respectively. As can be seen, K_L (0.019 L.mg^{-1}) deduced from the Langmuir isotherm is smaller than K_{LH} deduced from photocatalytic degradation. According to the Langmuir-Hinshelwood model, if K_{LH} truly reflected the adsorption affinity of the dye on the TiO_2 surface, K_L and K_{LH} would be identical. However, in other studies, it was reported that K_{LH} could be substantially larger than K_L , 280 times for metobromuron, 13 times for benzylic alcohol, 220 times for 4-chlorophenol (Vulliet *et al.*, 2003). Various explanations have been suggested: (i) a photoadsorption could occur (Lin *et al.*, 2006b) and (ii) the reaction could take place not only at the surface but also in the bulk solution (Vulliet *et al.*, 2003).

The effect of catalyst loading on degradation efficiency was investigated by varying the amount of catalysts ranging from 0.25 to 1.00 g.L^{-1} . The initial concentration of DB38 was kept constant during these experiments (100 mg.L^{-1}). Figure 7 shows the influence of the amount of TiO_2 in the reactor on the photodegradation rate of DB38. An increase in the rate of degradation was observed with increasing amounts of catalyst as the number of photons absorbed and the number of molecules adsorbed also increased. However this increase varied slightly, from 0.79 to $1.06 \text{ mg.L}^{-1}.\text{min}^{-1}$ when considering the greater variation in the concentration of catalyst (0.25 to 1.00 g.L^{-1}), which proves the use larger quantities of catalyst unnecessary.

IV. CONCLUSIONS

The TiO_2 nano material was prepared successfully through a low temperature hydrothermal process. The synthesized material presented a pure phase anatase, with high surface area and a crystal size on the nanometric scale. An evaluation of dye adsorption using TiO_2 showed that that the adsorption isotherm obtained followed the S-type in terms of the Giles classification. Various thermodynamic parameters have been calculated (ΔS° , ΔH° and ΔG°) indicating that the adsorption process is endothermic in nature and nonspontaneous. The oxide produced showed efficient catalytic activity in degrading the azodye in aqueous solution which was similar to that of commercially available TiO_2 photocatalyst (P25 Degussa).

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