

# STUDY OF THE PHOTOCATALYTIC DEGRADATION OF A CATIONIC DYE IN AQUEOUS SOLUTION BY DIFFERENT TYPES OF CATALYSTS

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## Résumé

La dégradation photocatalytique d'un colorant cationique: le Vert de Malachite Oxalate (MG), en présence des rayonnements UV-A à  $\lambda_{max}= 365$  nm a été étudiée en utilisant trois types de catalyseurs:  $TiO_2$ -P25,  $TiO_2$ -PC100 et le ZnO. L'adsorption de MG sur le  $TiO_2$ -P25 et le ZnO est bien décrite par le modèle de Langmuir, alors que le modèle de Freundlich représente mieux l'adsorption du MG sur le  $TiO_2$ -PC100. La disparition du MG par photocatalyse en présence des trois catalyseurs suit la cinétique de pseudo premier ordre, et le modèle de Langmuir-Hinshelwood est bien adapté pour décrire la cinétique de sa disparition. L'effet de la concentration initial en colorant, le type de catalyseur, l'addition de l'alcool et le pH de la solution sur la dégradation photocatalytique du MG en présence des trois catalyseurs a été discuté. Le ZnO a montré une meilleure réactivité photocatalytique pour la dégradation de MG par rapport au  $TiO_2$ -P25 et  $TiO_2$ -PC100 dans les différentes conditions étudiées. Les analyses de la DCO montrent, après 2 h d'irradiation, une minéralisation complète du MG en présence du ZnO, et une diminution de 42 % et 10 % en présence du  $TiO_2$ -P25 et  $TiO_2$ -PC100, respectivement.

**Mots-clés:** Colorant, Photolyse, UV, Photocatalyse, Décoloration, Catalyseur.

## Abstract

The photocatalytic degradation of an aqueous solution of Malachite Green Oxalate (MG) has been investigated using  $TiO_2$ -P25,  $TiO_2$ -PC100 and ZnO as catalysts in slurry form in presence of UV lamp at  $\lambda_{max}= 365$  nm. The adsorption of MG on  $TiO_2$ -P25 and ZnO catalysts was found favorable by the Langmuir approach, while Freundlich equation represents better the adsorption of MG on the  $TiO_2$ -PC100 surface. The disappearance of MG by photocatalysis in presence of the three catalysts followed pseudo first-order kinetics and Langmuir-Hinshelwood model is well suited to describe the kinetics of photocatalytic disappearance of these dye. The effect of the initial dye concentration, type of catalysts, addition of alcohol such as tert-butyl and solution pH on the degradation of MG in presence of  $TiO_2$ -P25,  $TiO_2$ -PC100 or ZnO catalysts were discussed. The ZnO catalyst is more effective than  $TiO_2$ -P25 and  $TiO_2$ -PC100 at different operating conditions studied. COD analysis showed a complete mineralization of the dye in a relatively short time of about 2 h for ZnO, and a reduction of 42 % and 10 % in COD for  $TiO_2$ -P25 and  $TiO_2$ -PC100, respectively, after 2 h of irradiation.

**Keywords:** Dye; Adsorption; Photocatalysis; Decolorization;  $TiO_2$ ; ZnO.

## ملخص

الهدف من هذا العمل هو دراسة الإزالة الفوتوتحفيزية لمحلول مائي لملون: المالايشيط الاخضر الاوكزالاتي (MG), باستعمال محفزات مختلفة و هي:  $TiO_2$ -P25,  $TiO_2$ -PC100, ZnO بوجود إشعاعات فوق بنفسجية  $\lambda_{max}= 365$  nm. إمتزاز MG على  $TiO_2$ -P25 و ZnO يتبع نموذج Langmuir, بينما نموذج Freundlich يعبر أفضل عن إمتزاز MG على  $TiO_2$ -PC100. إزالة MG بواسطة الطريقة الفوتوتحفيزية بوجود المحفزات الثلاث تتم وفق حركية من الدرجة الأولى و هذه الحركة تتبع نموذج Langmuir-Hinshelwood. المحفز ZnO هو أكثر فعالية من  $TiO_2$ -P25 و  $TiO_2$ -PC100 في الشروط المختلفة التي تمت دراستها, خلال هذا العمل تمت مناقشة تأثير كل من: تركيز الملونات, نوع المحفز, إضافة الكحول و درجة الحموضة على الإزالة الفوتوتحفيزية للملون في وجود كل من المحفزات الثلاث. قيم DCO تؤكد أن العملية الفوتوتحفيزية تؤدي إلى خفض المواد العضوية من الملونات إلى غاية التمعدن الكلي (minéralisation) في ظرف ساعتين بالنسبة لـ ZnO, و انخفاض بنسبة 42 % و 10 % بالنسبة لـ  $TiO_2$ -PC100 و  $TiO_2$ -P25 بعد ساعتين من العملية.

**الكلمات الرئيسية:** الملون, الإمتزاز, الفوتوتحفيزية, المحفز,  $TiO_2$ , ZnO.

## Introduction

Dyes are widely used in the textile, paper, plastics, leather, food and cosmetic industries to color their products. These processing industries are putting a severe burden on the environment, through the release of heavily polluted wastewaters. The removal of the non-biodegradable organic chemicals is a crucial ecological problem. Cationic dyes are model compounds of a series of common water soluble dyes that are generally toxic and resistant to destruction by biological and physico-chemical treatment methods. There is great demand of technology to decolorize the highly colored dye wastewater more effectively. There were reports of successful color removal from cationic dye wastewater using advanced oxidation processes (AOPs). Heterogeneous photocatalysis by semiconductor particles are a promising technology for the reduction of global environmental pollutants. Inorganic photocatalysts, such as TiO<sub>2</sub> and ZnO, have shown to be a relatively cheap and effective way of removing organic compounds and pollutant gases [1]. Titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO) are important photocatalysts and as such have been extensively studied for the removal of organic compounds from contaminated air and water and for microbial disinfection. TiO<sub>2</sub> semiconductor is the most used due to its good chemical and photochemical stability, it exhibits high photocatalytic activity, it is non-toxic and it is abundant and cheap [2]. However, ZnO appears to be a suitable alternative to TiO<sub>2</sub> since its photodegradation mechanism has been proven to be better or similar to that of TiO<sub>2</sub> [3]. ZnO has been reported to be more efficient than TiO<sub>2</sub> for the photooxidation of 2-phenylphenol and photocatalysed oxidation of phenol [4]. The biggest advantage of ZnO in comparison with TiO<sub>2</sub> is it absorbs over a larger fraction of UV spectrum and the corresponding threshold of ZnO is 425 nm [5]. In contrast, ZnO has the disadvantage that it is susceptible to dissolution process during the heterogeneous photocatalytic process.

Malachite Green Oxalate (MG), a cationic dye, widely used as a counter stain for paraffin embedded botanical material and staining bacterial polysaccharides and spores. Also used as a contrast stain in the Ziehl-Neelsen procedure. In the present work, the photocatalytic degradation of MG has been investigated

in aqueous solution containing three different catalysts: TiO<sub>2</sub>-P25, TiO<sub>2</sub>-PC100 and ZnO using UV-A light.

The aim of the present study is to investigate the degradation of aqueous solutions of MG, by photocatalysis using immobilized catalysts TiO<sub>2</sub> (TiO<sub>2</sub>-P25, TiO<sub>2</sub>-PC100) and ZnO. The kinetics and isotherms of adsorption of MG on catalysts was studied. The effects of operational parameters such as the initial dye concentration, type of catalysts, presence of alcohol such as tert-butyl and solution pH on photocatalytic degradation of MG in presence of TiO<sub>2</sub> and ZnO catalysts were investigated, and COD changes were also monitored.

## 2. Materials and methods

Malachite Green Oxalate (C.I. 42000), 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N, N-dimethylaniline supplied by Sigma-Aldrich, its chemical formula is C<sub>28</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>. The chemical structure of MG is shown in Fig. 1. The physicochemical data of ZnO, TiO<sub>2</sub>-P25 and other TiO<sub>2</sub> Millennium PC500, PC105, PC100 and PC50 used in this study are given in Table 1. The solutions were prepared with water from a Millipore Milli-Q water purification system. The adjustments of pH were realized using H<sub>2</sub>SO<sub>4</sub> from Merck and NaOH from Carlo Erba.

Adsorption experiments were performed in a circulating photoreactor made of pyrex open to air. The mixture was magnetically stirred to maintain even distribution of suspension throughout the reactor and eliminated mass gradient. The experiments of photocatalysis were carried out in the same reactor, fitted with four low pressure mercury UV lamps type Philips HPW. The light source has maximum intensity at 365 nm. At specific time intervals, samples were withdrawn from the bulk solution. The samples were filtered through a

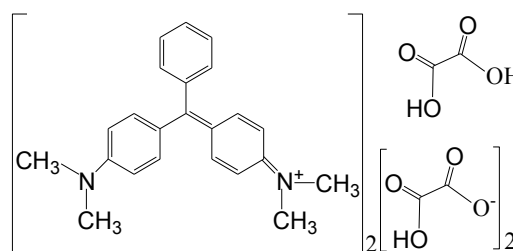


Fig.1. Chemical structure of MG.

Table 1. Chemical and physical properties of the photocatalysts.

Catalyst	Composition (%) Anatase / Rutile	Specific surface (m <sup>2</sup> /g)	Particle size (nm)	pH (10% wt)	Density (Kg/m <sup>3</sup> )
P25	80 / 20	55	30	3.0-4.0	3800
PC50	100	45 ± 5	20-30	2.5-4.5	-
PC100	100	80 - 100	15-25	1.5-3.5	600-900
PC105	100	75 - 95	15-25	3.5-5.5	600-900
PC500	100	250 >	5-10	5.0-7.5	-
ZnO	-	5	20-30	-	5606

Millipore filter 0.45  $\mu\text{m}$ . In order to compare the efficiency of the photocatalytic degradation of MG, the filtrates were analyzed by UV-Visible spectrometry using a UNICAM HELIOS  $\alpha$  UV-visible spectrophotometer at the maximum absorption wavelength of MG (616 nm). COD analysis was done by the Thomas and Mazas method [6].

### 3. Results and discussion

#### 3.1. Adsorption of MG on photocatalyst surface

Adsorption of pollutants on the semiconductor surface is an important parameter in heterogeneous photocatalysis. Therefore, it is important in a first step, to determine the adsorption isotherm using various concentrations of dye in order to evaluate the adsorption equilibrium constants of this dye on the photocatalyst. The amount of dye adsorbed onto  $\text{TiO}_2$  and ZnO (mg/g) was calculated using the following relationship:

$$Q_{ads} = \frac{(C_o - C_t) \cdot V}{m} \quad (1)$$

where  $Q_{ads}$  is the adsorbed quantity at time  $t$  (mg/g),  $C_o$  is the initial concentration of the substrate (mg/L),  $C_t$  is the concentration of the substrate (mg/L) at the moment  $t$  of the adsorption process,  $V$  is the volume of the solution (L) and  $m$  is the mass of adsorbent (g).

##### 3.1.1. Kinetic and equilibrium of adsorption of MG on photocatalysts surface

Adsorption tests in dark conditions were carried out in order to evaluate the equilibrium constants of the adsorption of dye on the photocatalyst. At natural pH, the kinetics of adsorption of MG at 10 mg/L on  $\text{TiO}_2$  at 1g/L ( $\text{TiO}_2$ -P25,  $\text{TiO}_2$ -PC100) in the range of concentration studied were fast, the equilibrium was reached after 30 min. The total amount of dye adsorbed on the photocatalysts materials, at natural pH, is equal to 3.72 mg/g for  $\text{TiO}_2$ -P25 and 1.62 mg/g for  $\text{TiO}_2$ -PC100. MG is more adsorbed on the  $\text{TiO}_2$ -P25 than on  $\text{TiO}_2$ -PC100 surface. In contrast, the amount of dye adsorbed on the ZnO does not reach a plateau.

##### 3.1.2. Isotherms of adsorption of MG on photocatalysts surface

The most common models to describe adsorption process are the parameter isotherms of Langmuir and

Freundlich. The following linearized Langmuir and Freundlich equations were used to fit the experimental data (Fig.2 (a) and (b)):

$$\frac{1}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{Q_{max}K_L C_e} \quad (2)$$

$$\ln Q = \ln K_f + (1/n) \ln C_{eq} \quad (3)$$

where  $Q_e$  is the specific adsorbed quantity of a model compound and  $C_e$  is the pollutant concentration, both at equilibrium;  $Q_{max}$  is the saturation (maximum) adsorption capacity and  $K_L$  is the adsorption constant.  $F$  and  $1/n$  are empirical factors and represent the Freundlich parameters.

The values of the Langmuir ( $Q_{max}$ ,  $K_L$ ) and Freundlich ( $F$ ,  $1/n$ ) parameters for the adsorption of MG on the three catalysts are calculated from the plots in Fig. 2 (a) and (b), respectively; and according to Eq. (2) and (3). These values are given in Table 2. The correlation coefficients indicated that Langmuir model is the more efficient to fit the experimental MG adsorption isotherm on  $\text{TiO}_2$ -P25 and ZnO, while Freundlich equation represents better the adsorption of MG on the  $\text{TiO}_2$ -PC100 surface. On the basis on the maximum adsorption capacity values, it's clear that ZnO ( $Q_{max}$ = 80 mg/g) has a greater capacity to adsorb the dye than  $\text{TiO}_2$ -P25 ( $Q_{max}$ = 19.68 mg/g) and  $\text{TiO}_2$ -PC100 ( $Q_{max}$ = 02.19 mg/g), while the adsorption capacity of  $\text{TiO}_2$ -PC100 was relatively lower. The values of  $1/n$  less than 1 show the favorable nature of adsorption of MG on the three catalysts [7].

#### 3.2. UV-visible spectrophotometry

The UV-vis absorption spectra from 200 to 800 nm of a MG solution at natural pH (pH= 6.9) shows three absorption maxima, as shown in Fig.3, one band in ultraviolet region at 318 nm and two in visible region at 426 nm and 616 nm. The principal band at 616 nm is due to the chromophore responsible for the characteristic color of this dye, and its decrease was used to monitor the decolorization of the MG dye.

The other absorbance in ultraviolet region is due to the  $\pi \rightarrow \pi^*$  transition in the aromatic ring, representing the aromatic content of the MG, and its decrease was used to monitor the degradation of aromatic part of the MG dye.

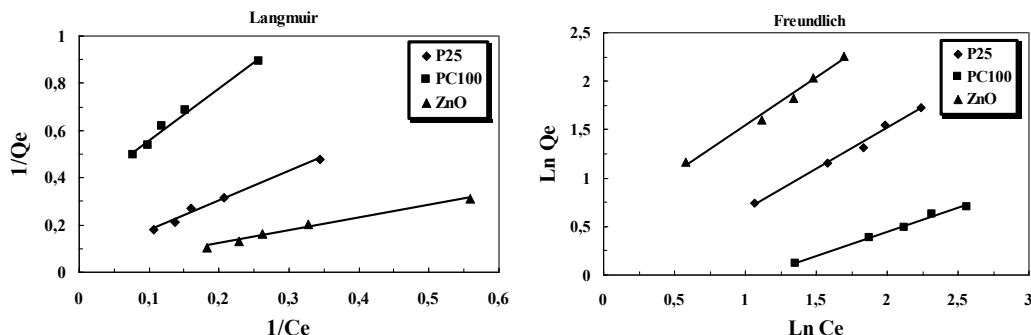


Fig.2. Adsorption isotherms of MG on  $\text{TiO}_2$ -P25,  $\text{TiO}_2$ -PC100 and ZnO: (a) Langmuir, (b) Freundlich, [Catalyst]= 1 g/L at natural pH= 6.9.

Table 2. Langmuir and Freundlich parameters

Catalyst	Langmuir		Freundlich			
	$Q_{max}(mg/g)$	$K_L(L/mg)$	$R^2$	$K_F(mg/g(L/mg)^{1/n})$	$1/n$	$R^2$
P25	19.68	0.040	0.991	0.833	0.85	0.989
PC100	02.19	0.153	0.990	0.570	0.50	0.994
ZnO	80.00	0.023	0.988	1.750	0.98	0.987

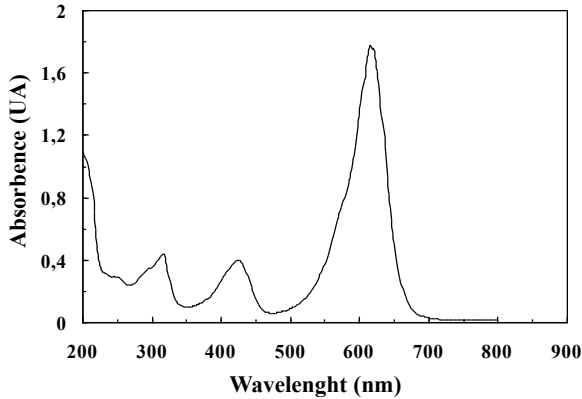


Fig.3. Absorbance spectra of MG: ([MG]= 10 mg/L, at natural pH= 6.9).

### 3.3. Preliminary experiments: photolysis and photocatalysis of MG

Fig. 4 shows the change in concentration of an aqueous solution of MG (10 mg/L) in the absence and presence of the photocatalyst (TiO<sub>2</sub>-P25, TiO<sub>2</sub>-PC100 or ZnO, 1 g/L). It has been observed that only a slight degradation takes place when the irradiation was carried out in the absence of catalyst. Whereas, the MG concentration was completely removed after 20 and 90 min of irradiation in presence of ZnO and TiO<sub>2</sub>-P25, respectively. The photodecay of MG using TiO<sub>2</sub>-PC100 is relatively slow in comparison with UV/ZnO and UV/TiO<sub>2</sub>-P25 systems.

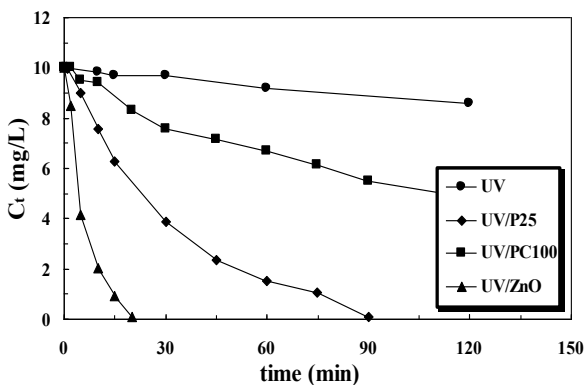


Fig.4. Evolution of MG concentration: ([MG]= 10 mg/L, [Catalyst]= 1 g/L, I= 2.5 mW/cm<sup>2</sup> and at natural pH= 6.9).

The degradation experiments by UV irradiation of MG aqueous solutions containing TiO<sub>2</sub>-P25, TiO<sub>2</sub>-PC100 or ZnO follow the pseudo-first-order kinetic law with respect to the concentration of the dye in the solution (Fig.5), according to the equation:

$$\ln\left(\frac{C_0}{C_t}\right) = k_{app}t \quad (4)$$

where  $C_0$  is the initial concentration of MG (mg/L),  $C_t$  is the instant concentration in the sample at time  $t$  (mg/L),  $k_{app}$  is the apparent pseudo-first-order reaction rate constant (min<sup>-1</sup>) and  $t$  is the reaction time (min). A plot of  $\ln(C_0/C_t)$  versus  $t$  will yield a slope of  $k_{app}$ .

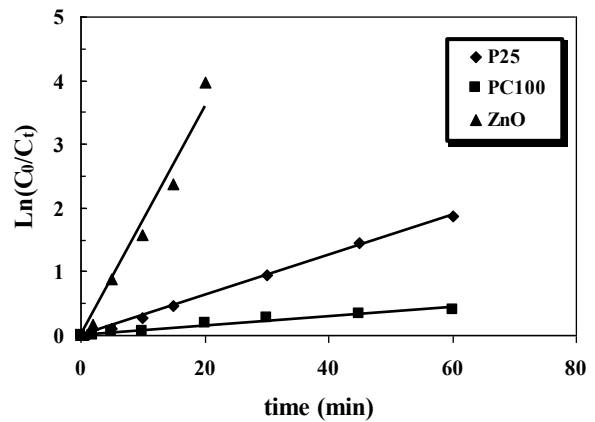


Fig.5. Plot of  $\ln(C_0/C_t)$  as a function time for MG photodegradation:([Catalyst]= 1g/L, I= 2.5 mW/cm<sup>2</sup> at natural pH= 6.9).

### 3.4. Factors influencing the photocatalytic degradation

#### 3.4.1. Effect of initial dye concentration

The effect of initial dye concentration on the photocatalytic degradation process of MG on TiO<sub>2</sub>-P25, TiO<sub>2</sub>-PC100 and ZnO has been studied in a range between 5 to 15 mg/L at natural pH for a constant catalysts amount (1 g/L) and a constant photonic flux (2.5 mW/cm<sup>2</sup>). The results showed that the rate constants decrease with increase in the initial dye concentration as shown in Fig. 6. This may be attributed to several factors. At higher dye concentrations, there would be more adsorption of dye on catalysts resulting in a lesser availability of catalyst surface for hydroxyl radical generations. Similar results have been reported for the photocatalytic oxidation of other organic pollutants [8-10]. One reason for this result is the covering of catalyst surface with dye ions what suppresses the generation of hydroxyl radicals. Another possible explanation might be the UV-screening effect of the dye itself. At high dye concentrations, a significant portion of UV light might be absorbed by the dye molecules rather than the TiO<sub>2</sub> particles. This

phenomenon reduces the efficiency of the catalytic reaction because the concentrations of  $\bullet\text{OH}$  and  $\text{O}_2^{\bullet-}$  decrease [11]. Many authors [13-15] have also used Langmuir–Hinshelwood (L–H) kinetic model to analyze heterogeneous photocatalytic reactions in terms of the concentration of the target molecule. The model is also rationalized for our experimental results by the following equation:

$$r = -\frac{dC}{dt} = k_{app}C_e = k_{LH}\theta = \frac{k_c K_{L-H} C_e}{1 + K_{L-H} C_e} \quad (5)$$

$$\theta = \frac{K C_e}{1 + K C_e} \quad (6)$$

where  $k_{app}$  is the pseudo-first-order reaction rate constant ( $\text{min}^{-1}$ ),  $k_c$  is the reaction rate constant at the surface,  $K_{L-H}$  is the Langmuir–Hinshelwood equilibrium adsorption coefficient,  $K$  is the adsorption constant and  $\theta$  is the surface coverage of catalyst.

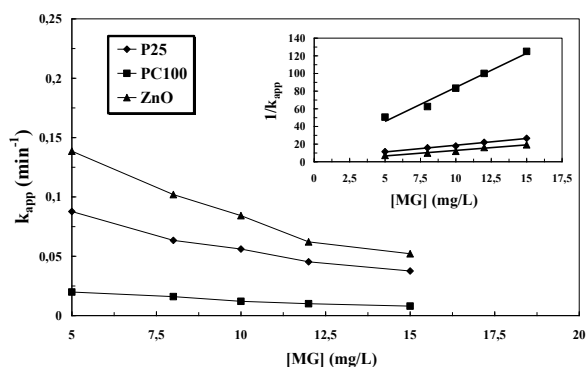


Fig.6. Effect of initial concentration on the photo decolorization rate of MG. In the inset: Representation of Langmuir–Hinshelwood equation: ([Catalyst]= 1g/L, I= 2.5 mW/cm<sup>2</sup> at natural pH= 6.9)

Table 3. Langmuir–Hinshelwood constants.

Catalyseur	$K_r(\text{mg/Lmin})$	$K_{L-H}(\text{L/mg})$	$R^2$
P25	0.654	0.441	0.992
PC100	0.130	1.084	0.980
ZnO	0.800	3.660	0.961

The linear form of Langmuir–Hinshelwood model, in the following expression, translates the dependence of  $1/k_{app}$  values on the respective  $C_e$  values of MG concentrations:

$$\frac{1}{k_{app}} = \frac{1}{k_c K_{L-H}} + \frac{C_e}{k_c} \quad (7)$$

The applicability of L–H equation for MG photodegradation in presence of TiO<sub>2</sub>-P25, TiO<sub>2</sub>-PC100 or ZnO has been confirmed by the linear plot obtained by plotting the reciprocal of first order rate constant ( $1/k_{app}$ ) against initial concentration ( $C_e$ ) as shown in the

inset in Fig. 6. The values of  $K_{L-H}$  and  $k_c$  of the three photocatalysts are shown in Table 3. The constant of adsorption calculated from the Langmuir–Hinshelwood model ( $K_{L-H}$ ) is different to that calculated from adsorption isotherm ( $k_L$ ), the value of the calculated adsorption coefficient  $K$  for photocatalytic degradation was about 11, 7 and 159 times higher than the adsorption constant  $K_L$  in the dark for TiO<sub>2</sub>-P25, TiO<sub>2</sub>-PC100 and ZnO, respectively. The value of the adsorption constant indicates that the adsorption plays a role in the photocatalytic reaction. There have been several studies reporting that  $K_{LH}$  could be substantially larger than  $K_L$ : 12 times for monochlorobenzene [16], 220 times for 4-chlorophenol [17]. A possible explanation is that the irradiation modifies adsorptive sites, and the consequence is that  $K_{LH}$  measured under irradiation is different from  $K_L$  measured in the dark.

The evolution of the surface coverage of catalysts  $\theta$  as function of concentration is shown on Fig.7; under irradiation:  $\theta_{UV}$  = Number of occupied active sites/ Number total of active sites and in obscurity:  $\theta_{obs}$  = Number of occupied adsorption sites/ Number of total adsorption sites. For all concentrations of dye from 5 to 15 mg/L and with the three catalysts,  $\theta_{UV}$  was superior from  $\theta_{obs}$ ; this finding may be explained by considering that under irradiation there is an increase of the number of occupied sites: photoadsorption.

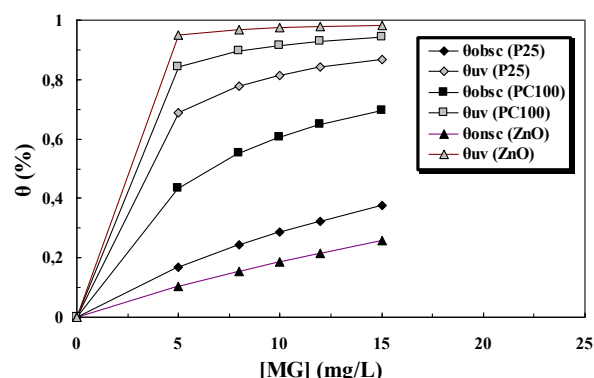


Fig.7. Evolution of the surface coverage of catalysts  $\theta$  as function of concentration of MG: ([Catalyst]= 1g/L, I= 2.5 mW/cm<sup>2</sup> at natural pH= 6.9).

### 3.4.2. Effect of addition of tertio-butyl alcohol

It is expected that the photodegradation of MG would mainly occur by hydroxyl radical attack. In order to investigate the dependence of the hydroxyl radical during the degradation of MG by photocatalysis with TiO<sub>2</sub>-P25, TiO<sub>2</sub>-PC100 and ZnO as catalysts on suspension, the photocatalytic degradation of MG in presence of tert-butyl alcohol, known as an effective hydroxyl radical scavenger, was performed. As shown in Fig.8, a small amount of tert-butyl (1% and 6%) inhibited the photocatalytic degradation of MG in presence of TiO<sub>2</sub>-P25 or ZnO catalysts. The retarding effect of tert-butyl in the systems UV/TiO<sub>2</sub>-P25 and UV/ZnO can be explained by OH competitive reactions with MG and tert-butyl. This result showed that

hydroxyl radicals play a major role during these tow process [3] and [4]. However, the photocatalytic degradation of MG with TiO<sub>2</sub>-PC100 catalyst was not affected by the presence of the radical scavenger. These results clearly suggest that the positively charged holes play the predominant role in the photodegradation of MG by the UV/PC100 process.

### 3.4.3. Effect of various kinds of photocatalysts

In order to compare the reactivity of ZnO, TiO<sub>2</sub>-P25 and TiO<sub>2</sub>-PC100 to the photodegradation of MG with other TiO<sub>2</sub> Millennium, the photodegradation of

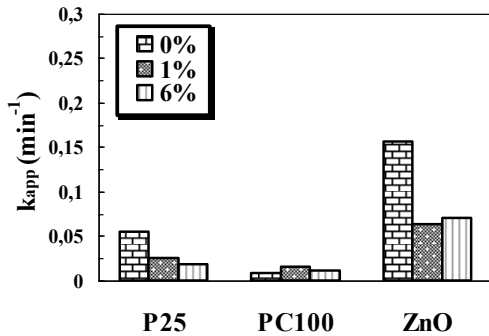


Fig.8. Effect of tert-butyl alcohol on the photocatalytic degradation of MG: ([MG]=10 mg/L, [TiO<sub>2</sub>]= 1 g/L, I= 2.5 mW/cm<sup>2</sup> and at natural pH).

MG (10 mg/L) with various kinds of TiO<sub>2</sub> Millennium such as: PC50, PC105 and PC500 (1g/L) at natural pH and an incident photonic flux of 2.5 mW/cm<sup>2</sup> has been studied. The physico-chemical characteristics of these photocatalysts are reported in Table 1. For all these experiments, photocatalytic degradation of MG followed pseudo first-order decay kinetics and the apparent constants are presented in Fig.9. ZnO has shown more reactivity then all TiO<sub>2</sub> catalysts because it absorbs over a larger fraction of UV spectrum and the corresponding threshold of ZnO is 425 nm [5].The efficiency of photocatalysts for the degradation of MG was shown to follow the order: P25> PC500> PC50> PC105> PC100. TiO<sub>2</sub>-P25 is more active than other Millennium photo-catalysts. Although, TiO<sub>2</sub>-P25 present the lowest surface its photo-reactivity is larger than the other TiO<sub>2</sub> Millennium, this result may be due to the slow recombination of e<sup>-</sup> - h<sup>+</sup> pairs in the case of TiO<sub>2</sub>-P25 [23].There is no apparent correlation between the photocatalytic activity and the surface area and particle size of photocatalysts for the degradation of MG (specific surface: PC500> PC100> PC105> P25> PC50 and particle size: P25> PC50> PC105> PC100> PC500). The differences in the photocatalytic activity can be related to the presence of impurities and the existence of structural defects in the crystalline framework or density of hydroxyl groups on the catalyst surface [24].

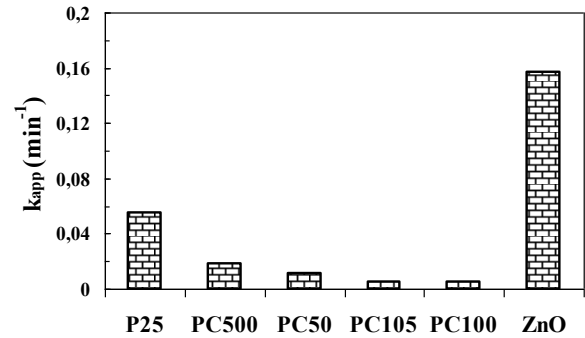


Fig.9. Effect of type of catalyst on the photocatalytic degradation of MG: ([MG]=10 mg/L, [Catalyst]= 1 g/L, I= 2.5 mW/cm<sup>2</sup> and at natural pH).

### 3.4.4. Influence of pH of solution

The most important parameter that influences the photocatalytic degradation is solution pH. pH is a complex parameter since it influences the surface charge properties of the catalyst and the charge of the dye molecules [25]. Effect of pH on the photocatalytic degradation of MG in presence of TiO<sub>2</sub>-P25, TiO<sub>2</sub>-PC100 and ZnO was studied from 1 to 12. For TiO<sub>2</sub>-P25 and TiO<sub>2</sub>-PC100, the point of zero charge (pH<sub>pzc</sub>) is about 6.25 [26]. This means that the TiO<sub>2</sub> surface would be positively charged in an acidic solution (TiOH<sub>2</sub><sup>+</sup> at pH < 6.25), negatively charged in an alkaline medium (TiO<sup>-</sup> at pH > 6.25), and neutral when the transition solution pH value is around 6.25. As seen in Fig. 10, the higher photocatalytic decolorization of MG in presence of TiO<sub>2</sub>-P25 and TiO<sub>2</sub>-PC100 occurs at a solution pH higher than the point of zero charge (pzc) of TiO<sub>2</sub>; when MG is dissolved in water, its structure becomes positively charged and these favors the adsorption of MG on the negatively charged TiO<sub>2</sub> surface and lead to enhancing the photocatalytic decolorization. For ZnO, the maximum degradation was observed at pH 10. In alkaline solutions photodegradation efficiency was more than that in acidic solutions. It can be due to more efficient formation of hydroxyl radicals in alkaline solution [27] and photodecomposition of ZnO in acidic solutions [4].

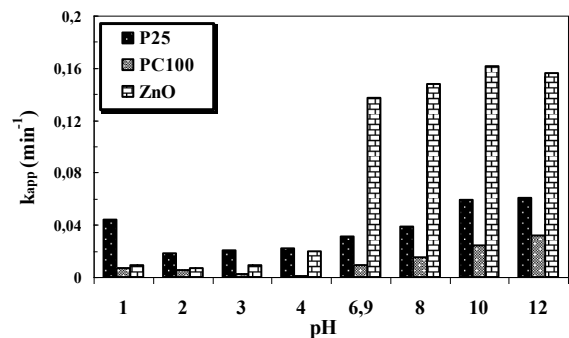


Fig.10. Effect of pH on the photocatalytic degradation of MG: ([MG]=10 mg/L, ([Catalyst]= 1g/L, I= 2.5 mW/cm<sup>2</sup>).

On the other hand, the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of ZnO particles is 8.6 [28], catalyst surface is positively charged in acidic media ( $\text{ZnOH}_2^+$  at  $\text{pH} < 8.6$ ) whereas it is negatively charged under alkaline condition ( $\text{ZnO}^-$  at  $\text{pH} > 8.6$ ). Meanwhile, MG is a cationic dye, so it is positively charged; therefore, the particles of MG could be adsorbed on the surfaces of ZnO particles easily above its  $\text{pH}_{\text{pzc}}$  and the photodegradation will be accelerated.

#### 3.4.5. COD removal–toxicity evolution

The complete decomposition to  $\text{CO}_2$  via photocatalytic reactions is of great significance in water treatment because it is the unequivocal evidence of the total destruction of organic compounds in water. For studying the degradation process of MG, the percentage change in COD was studied for the dye sample having initial concentration of 10 mg/L and photocatalyst loading 1 g/L as a function of irradiation time. The results of COD measurements obtained after 5h exposure time of the dye in presence of  $\text{TiO}_2\text{-P25}$ ,  $\text{TiO}_2\text{-PC100}$  and ZnO are presented in Fig. 11. The inset in Fig. 11 show a comparison of the decolorization and mineralization yields after 30 min of contact time.

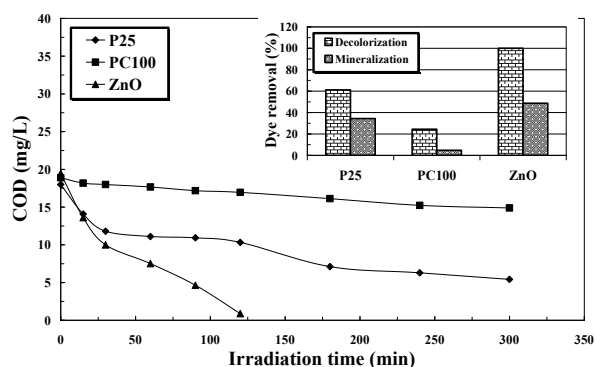


Fig.11. Kinetics of COD of the photocatalytic degradation of MG. In the inset: Comparison of the dye removal values between decolorization and mineralization: ( $[\text{MG}]=10$  mg/L,  $[\text{Catalyst}]=1$  g/L,  $I=2.5$   $\text{mW}/\text{cm}^2$ , at natural pH and contact time: 30 min).

It is obvious that decolorization of dye solutions is not followed by the same extent of mineralization. That means that the dye decomposes to smaller organic intermediates that are still present in the solution. Within a longer illumination period though, a significant removal of COD is accomplished (almost 95 % COD removal of MG in presence of ZnO catalyst was accomplished for 2h illumination). While, a partial decomposition of MG within the first 2 h was observed for  $\text{TiO}_2\text{-P25}$  (42.50 %) and  $\text{TiO}_2\text{-PC100}$  (10.30 %). However, an overall 70 % and 21.26 % reduction in COD is observed for  $\text{TiO}_2\text{-P25}$  and  $\text{TiO}_2\text{-PC100}$ , respectively, after 5h of irradiation as shown in Fig.11, which means that prolonged illumination can probably lead to complete mineralization.

## 4. Conclusion

The photocatalytic degradation of Malachite Green oxalate (MG) in aqueous solution was studied using  $\text{TiO}_2\text{-P25}$ ,  $\text{TiO}_2\text{-PC100}$  and ZnO as catalysts. The experimental results of adsorption show that Langmuir model is the more efficient to fit the MG adsorption on  $\text{TiO}_2\text{-P25}$  and ZnO, while Freundlich equation represents better the adsorption of MG on the  $\text{TiO}_2\text{-PC100}$  surface. The photo-oxidation of MG dye followed first order kinetics, which fitted the Langmuir–Hinshelwood model. Effective photocatalytic degradation of the MG dye is available with the three catalyst suspended aqueous solutions. The decolorization rate constant of dye decreases when the concentration of dye increases. Comparison of photocatalytic activity of different semiconductors has clearly indicated that the ZnO is the most active photocatalyst for decolorization of MG.  $\text{TiO}_2\text{-P25}$  is more active than other  $\text{TiO}_2$  Millennium photo-catalysts for decolorization of MG, these may be due to its slow recombination of  $e^-h^+$  pairs. As our results showed that tert-butyl inhibited the photodegradation of dye in presence of  $\text{TiO}_2\text{-P25}$  and ZnO, we concluded from the inhibitory effect of tert-butyl that hydroxyl radicals play a major role in photocatalytic degradation of MG. However, the photocatalytic degradation of MG with  $\text{TiO}_2\text{-PC100}$  as catalyst was not affected by the presence of the radical scavenger; these results suggest that the positively charged holes play the predominant role in the photodegradation of MG by the UV/PC100 process. The higher photocatalytic decolorization of MG with the three catalysts occurs in alkaline medium, and ZnO cannot be used in acidic solution as a photocatalyst because of photodecomposition. The complete mineralization of the dye could be achieved in a relatively short time of about 2h for ZnO. While, a partial decomposition of MG within the first 2h was observed for  $\text{TiO}_2\text{-P25}$  (42.50%) and  $\text{TiO}_2\text{-PC100}$  (10.30%), and a prolonged illumination can probably lead to complete mineralization.

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