

ABSTRACT

The photoelimination, at ambient temperature, of aqueous solutions of Direct Red 80 dye (DR 80) in the presence of TiO₂ and ZnO catalysts has been studied in the presence of UV radiation generated by an artificial light source. We have determined the influence of several physico-chemical parameters (the mass of the catalyst, the initial concentration of dye and the initial pH of the solution) which govern the kinetics of degradation of this pollutant in order to be in optimum conditions. The catalysts used show a good photocatalytic activity. Indeed, for the first 15 minutes of irradiation, approximately 96% and 87% of the dye is eliminated in the presence respectively of TiO₂ and ZnO. The kinetics of photocatalytic degradation were investigated and modeled by the Langmuir-Hinshelwood equation, by which the k rate constant and the K_{LH} adsorption equilibrium constant were evaluated. The results showed that the pH significantly affects the process of the elimination of the dye. The maximum rate of degradation of DR 80 is observed at pH = 3

KEYWORDS: Water treatment, DR 80 dye, Heterogeneous photocatalysis, TiO₂, ZnO.

INTRODUCTION

Various industrial sectors such as the textile, paper, rubber, the food and pharmaceutical industries use dyes in the manufacture of their products [1]. The textile industry is one of the largest producers of liquid effluents, which contain dyes that does not bind on the fiber during the dyeing process [2]. These dyes can pollute water plans and change the biological cycles, by affecting the process of photosynthesis. In addition, they can also threaten human health during a prolonged contact with these products which can lead to toxic reactions such as skin allergy (dermatitis) and also affect the respiratory tract functions [3-5]. The most used classification of dyes is that of azo type. This large class includes the Direct Red 80 dye (DR 80). It is generally characterized by the presence of one or more azo group (-N=N-) and aromatic nuclei, which are considered as toxic and mutagenic to living organisms [6].

These toxic products are generally very poorly biodegradable. The Advanced Oxidation Processes (AOPs) are techniques that allow their total mineralization (transformation into water, carbon dioxide and / or inorganic ions) [7-10]. Among these AOPs, the heterogeneous photocatalysis revealed as a potential solution and emerging for the elimination of these compounds [11-14].

The work presented has for objective the study of the degradation by heterogeneous photocatalysis of diazo dye DR 80, using two semi-conductors TiO₂ and ZnO. Thus, the influence of a certain physico-chemical parameters such that the amount of catalyst, the initial concentration of dye and the pH of reaction medium on the adsorption capacity and on the elimination kinetics of the dye has been examined.

MATERIALS AND METHODS**Reagent**

The DR 80 dye (Figure 1) chosen in this study comes from the company Aldrich. It is used without any prior purification in distilled water. Its physico-chemical properties are shown in Table 1. The two carriers used in this

study are TiO₂ (P-25 : 80% anatase and 20% rutile) and ZnO which were provided respectively by the companies Degussa and Sigma Aldrich. The properties of these photocatalysts are listed in Table 2.

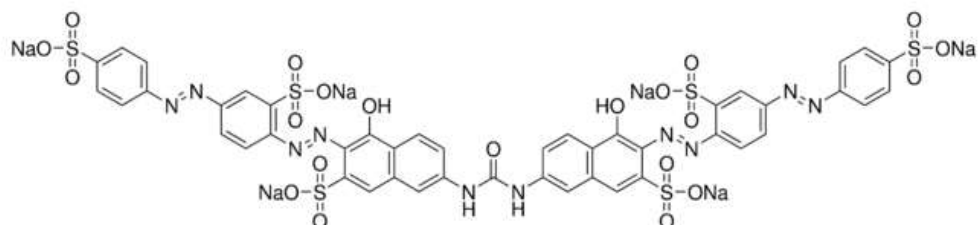


Figure 1 : Chemical structure of DR 80 dye.

Table 1 : Physico-chemical properties of the dye DR 80.

Type	Anionic
λ_{max} (nm)	527
Molar mass(g/mol)	1470
Solubility in water (g/l) à 25 °C	60
Famille	Direct dye
Chemical formula	C ₄₅ H ₂₆ O ₂₁ N ₁₀ S ₆ Na ₆

Table 2 : Main properties of TiO₂ and ZnO photocatalysts.

Properties	TiO ₂	ZnO
Density (g/cm ³)	3,85	5,6
Specific surface (m ² /g)	50	100
Energy Eg (eV)	3,2	3,2
λ_{max} (nm)	390	365
pH _{pcz}	6,8	8,9

Photoreactor

Experimental studies of the photocatalytic elimination of the DR 80 dye are performed in a reactor with a half-liter. The latter, is a photochemical reactor to immersion of cylindrical shape in Pyrex, which presents two side openings, one for introducing the oxygen and a second which serves to take samples. These dimensions are of the order 8 and 12 cm, respectively for the diameter and height (Figure 2). During the experiment, the mixture is maintained under continuous agitation (500 rpm) using a magnetic stirrer. Irradiation is performed by means of a mercury vapor lamp high pressure of 125 Watt (HPK-125 W Philips). The lamp is placed in a jacket of 2.5 cm in diameter and permanently cooled by a continuous flow of water.



Figure 2 : Photography of photoreactor used.

RESULTS AND DISCUSSION

Kinetic study of the adsorption of DR 80 on TiO₂ and ZnO

Adsorption Kinetics

During the photocatalytic degradation, it is necessary to study the phenomenon of adsorption before the irradiation because this is a crucial step before the irradiation. The adsorption kinetics of DR 80 on the two carriers TiO₂ and ZnO was realized in the initial pH of the solution at different initial concentrations of dye, with masses of 100 mg/L and 200 mg/L, respectively, for TiO₂ and ZnO.

Figures 3 and 4 illustrate the adsorption kinetics of the dye on TiO₂ and ZnO, and show that it is fast at the beginning of the process and becomes more and more slow during the time of agitation to achieve a level of balance to 30 min on the two catalysts. This time indicates that the adsorption equilibrium is reached. It is therefore imperative to leave the agitation of the mixture at least during this time before the irradiation of the mixture.

According to several authors [15, 16], the adsorption may be controlled by the step of transfer of the adsorbate through the external liquid film and /or the diffusion of the solute to the inside of the adsorbent particle.

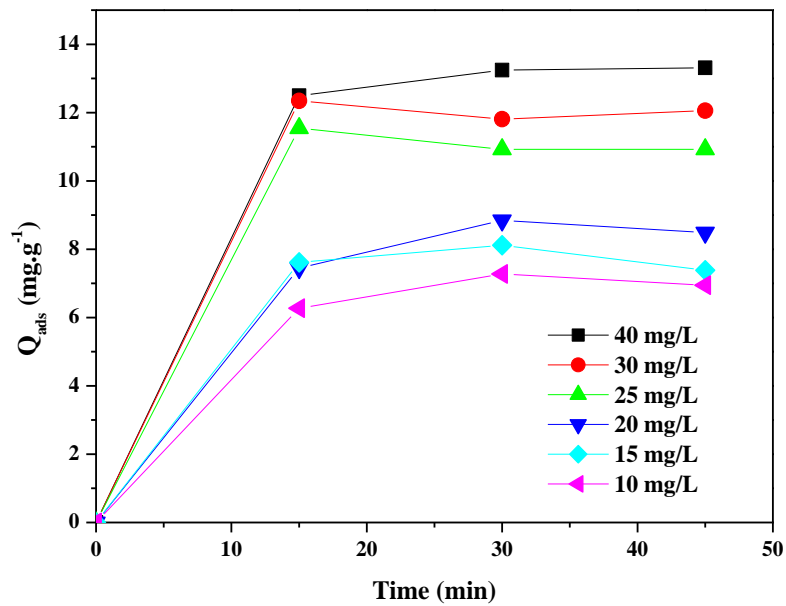


Figure 3 : Kinetics of adsorption of DR80 on ZnO at different initial concentration.

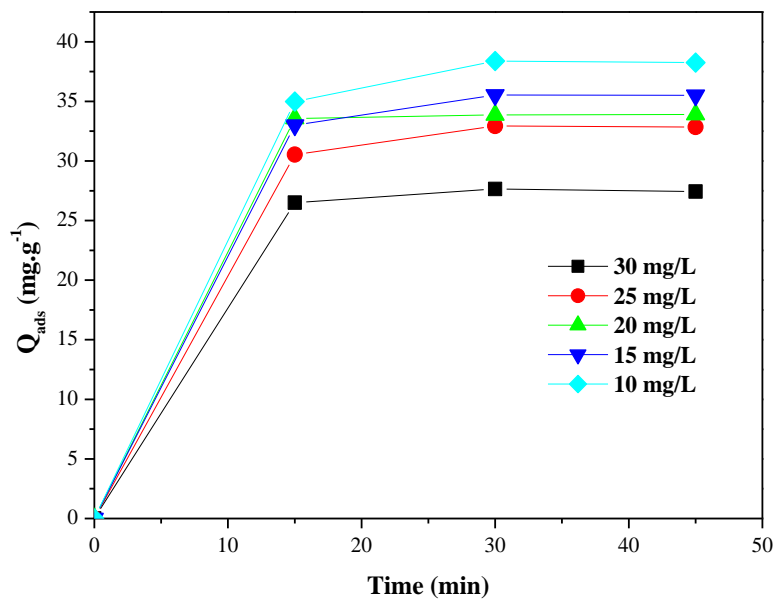


Figure 4 : Kinetics of adsorption of DR80 on ZnO at different initial concentration.

Adsorption isotherms

In order to determine the maximum capacity of adsorption of the dye on TiO₂ and on ZnO, we adopted the two models more common Langmuir and Freundlich for modeling the experimental values obtained in these phenomena of adsorption. These two adsorption isotherms represent the assessment of the amount adsorbed, depending of the equilibrium concentrations $Q_e = f(C_e)$ at a constant temperature (Figure 5). These representations of Langmuir and Freundlich were used to show the distribution of the DR 80 between the solid and liquid phases (the adsorbent and the solution) in equilibrium conditions.

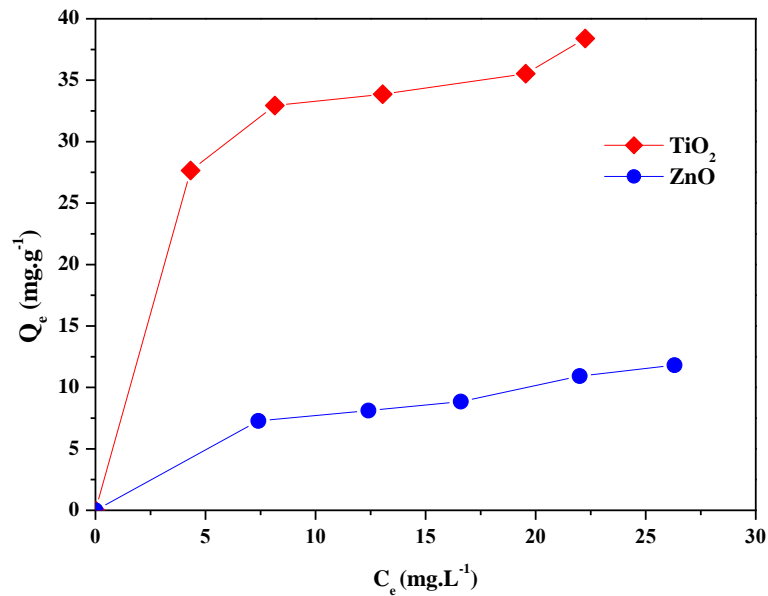


Figure 5 : Adsorption isotherm of the dye DR 80 on TiO₂ and ZnO.

The linear form of the Langmuir isotherm is given by the following equation:

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

Where Q_e (mg.g⁻¹) is the amount adsorbed at equilibrium, C_e (mg.L⁻¹) is the concentration at equilibrium, Q_{max} (mg.g⁻¹) is the maximum amount adsorbed and K_L (L.mg⁻¹) is adsorption equilibrium constant of Langmuir.

Two straight lines are obtained there drawing $1/Q_e$ in function of $1/C_e$ in the concentration range by dye ranging from 5 to 30 mg.L⁻¹ for TiO₂ and ZnO (Figure 6). The numerical values of Q_{max} and K_L calculated, respectively, from the intersection with the intercept and slope of the right to TiO₂ and ZnO, are represented on the Table 3. We note that the capacities of adsorption of DR 80 on the TiO₂ are more important in relation to the one on ZnO. This difference is due to the nature of TiO₂ and ZnO and also to the size of the each bracket with the molecule DR 80.

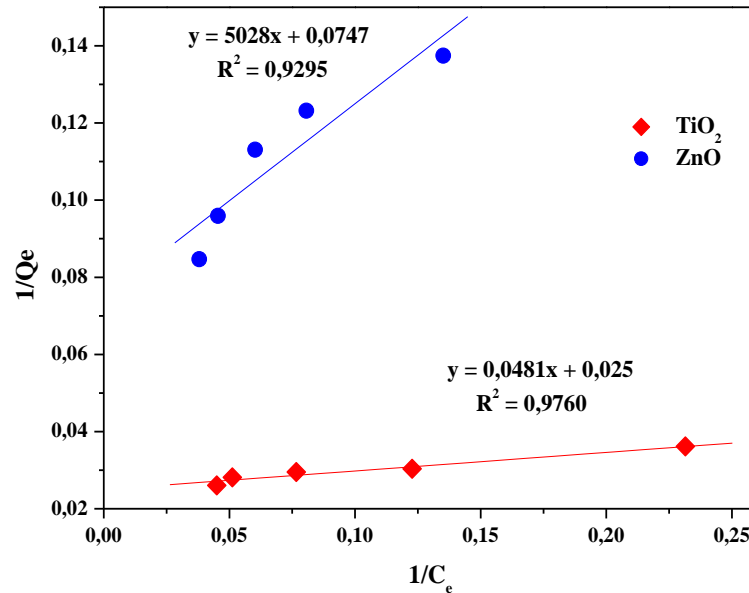


Figure 6 : Linear transformation of the Langmuir model on TiO₂ and ZnO.

The adsorption results were also modeled by applying the Freundlich model, which has as linear transformation the following equation:

$$\ln Q_e = \ln K_F + 1/n_F \ln C_e \quad (\text{Eq 2})$$

The graphic representation of $\ln Q_e$ in function of $\ln C_e$ for the two catalysts studied (TiO₂ and ZnO) gives a straight line (Figure 7). The kinetic parameters of adsorption of this model are grouped in the Table 3. A value of $1/n_F$ between 0 and 1 indicates a favorable adsorption [17]. According to our results, it appears that the adsorption of the dye DR 80 on the two catalysts is favorable. This table shows a linear correlation coefficient of R^2 of Freundlich better than that of Langmuir (ZnO) thus reinforcing the hypothesis of the model Freundlich and highlighting of heterogeneous sites of adsorption. As well, the Langmuir model presents a correlation coefficient R^2 better than that of the Freundlich model for the catalyst TiO₂, this indicates that the Langmuir isotherm better describes the adsorption than that of Freundlich and highlighting a single type of adsorption sites.

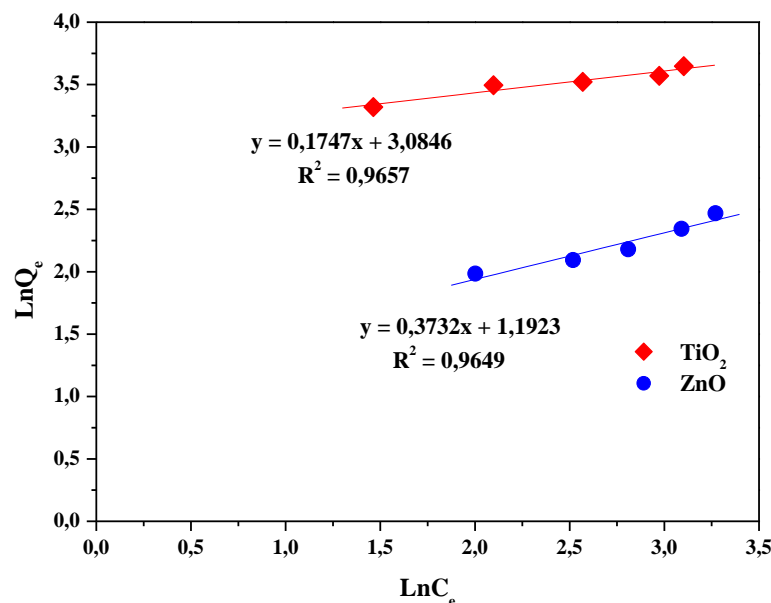


Figure 7 : Linear transformation of the Freundlich model on TiO₂ and ZnO.

Tableau 3 : Langmuir and Freundlich parameters for the adsorption on TiO₂ and ZnO

Isotherme parameters	Langmuir			Freundlich		
	Q _{max} (mg.g ⁻¹)	K _L (L.mg ⁻¹)	R ²	K _F (mg.g ⁻¹)	n _F	R ²
TiO ₂	40	0,52	97,60	21,86	5,72	96,57
ZnO	13,39	0,15	92,95	3,29	2,68	96,49

Photoelimination of DR 80

Effect of TiO₂ and ZnO concentration

The initial rates of the reaction are directly proportional to the concentration of the catalyst to reach a maximum value to approximately 100 mg/L and 200 mg/L, respectively on TiO₂ and ZnO. These limit values correspond to the optimal concentrations deductions where all grains of the catalyst TiO₂ or ZnO are photoactivated. This phenomenon is already observed in many studies [18, 19]. Indeed, above these values the initial rate of reaction becomes independent of the concentration of catalyst and the curve takes a form of a plate because of the saturation of the absorption of photons or by the loss of light by diffusion.

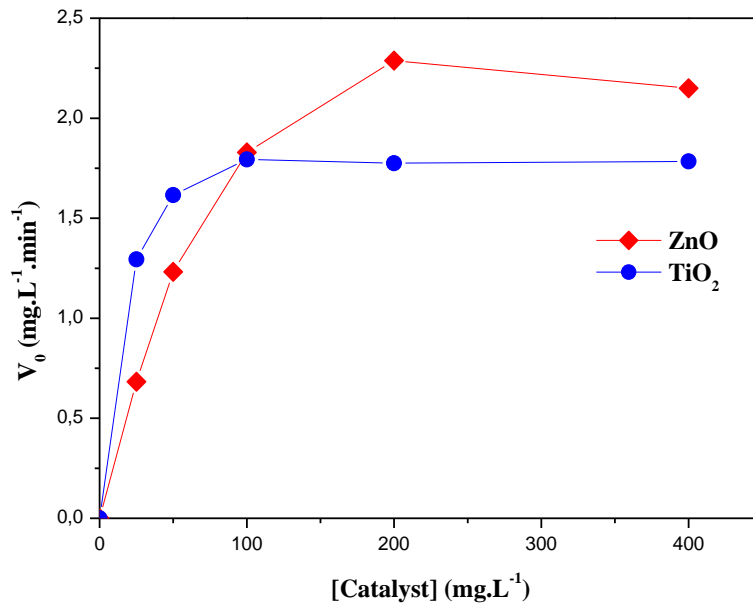


Figure 9 : Effect of TiO₂ and ZnO concentration on the disappearance kinetics of DR 80.

Effect of initial dye concentration

We have studied this effect by varying the initial DR 80 concentrations of 10 mg.L⁻¹ to 40 mg.L⁻¹, in the presence of the optimal mass of the catalyst 100 mg and 200 mg, respectively of TiO₂ and ZnO. Figure 10 shows that the dye DR 80, under irradiation is totally degraded for the different concentrations tested, when you irradiate the mixture. The time required for the total elimination varies as a function of the concentration. In addition, over the initial pollutant concentration is important, the more the time necessary to its disappearance is long.

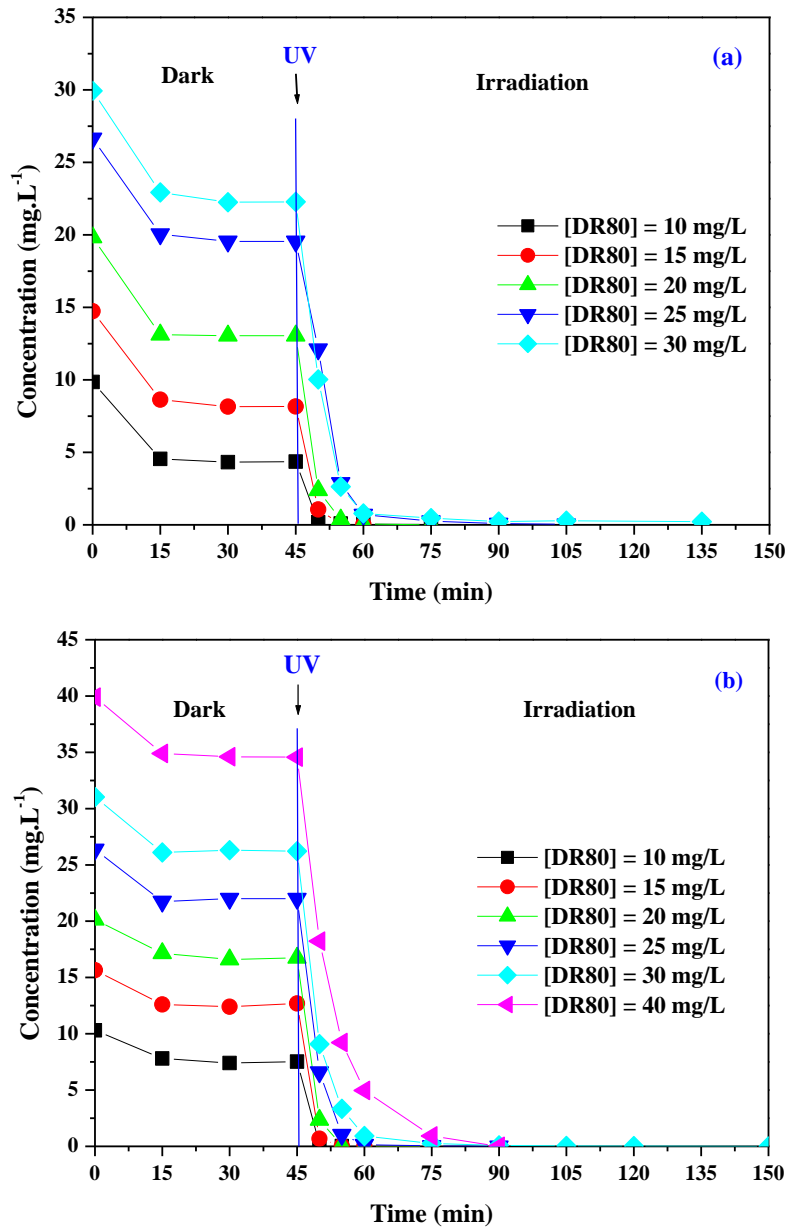


Figure 10 : Elimination kinetics of dye DR80 at different concentrations in the presence of TiO₂ (a) et ZnO (b).

The variations of the initial rate V_0 , depending on the increasing initial concentrations C_0 of the dye DR 80 (Figure 11), show that the rate of transformation increases rapidly at low concentrations and then tends toward a limit value equal to 2,55 mg/L.min and 2,36 mg/L.min, respectively on TiO₂ and ZnO. These values correspond to the saturation of the surface of two catalysts.

The linear transformed the equation of Langmuir-Hinshelwood expressed by the inverse of V_0 as a function of the inverse of C_0 is given by the following relationship:

$$\frac{1}{V_0} = \frac{1}{k} + \frac{1}{kK_{LH}C_0} \quad (\text{Eq 4})$$

This transformation gives a right with a correlation coefficient approaching unity for the degradation of DR 80 on the two catalysts. This shows that the reaction follows well the Langmuir-Hinshelwood model. The photodegradation of the dye thus occurs essentially at the surface of TiO₂ and ZnO solids. The values of the kinetic

constants observed have been determined graphically from the Figure 12 ($1/k \cdot K_{LH}$ represents the slope of the right and $1/k$ the intercept) and are listed in the Table 4.

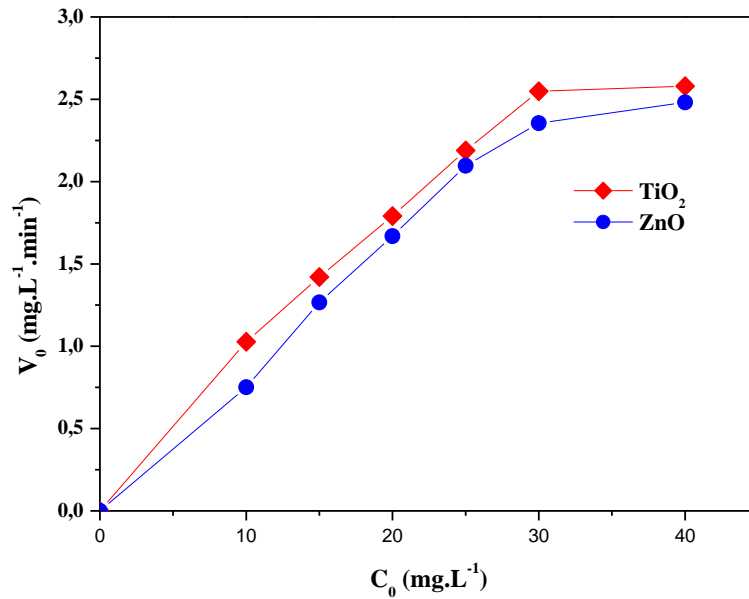


Figure 11 : Effect of the initial concentration on the initial rate of the removal photocatalytic of DR 80.

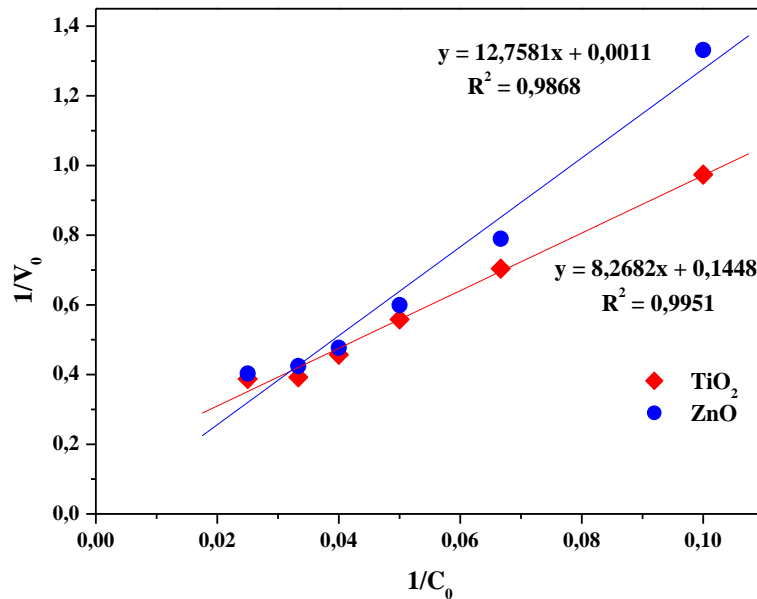


Figure 12 : Linearization of the Langmuir-Hinshelwood isotherm of DR 80.

Table 4 : Constants of the Langmuir-Hinshelwood model for the photoélimination of DR 80 on TiO₂ and ZnO.

parameters	k(mg/l.min)	K_{LH} (l/mg)	R^2
TiO ₂	6,906	$1,75 \cdot 10^{-2}$	0,9951
ZnO	$9,090 \cdot 10^2$	$8,62 \cdot 10^{-5}$	0,9868

Effect of initial pH

The pH is a parameter that determines both the state of the solid surface as well as the molecular state in which is the present compound in the solution. It can therefore affect the adsorption capacity of the solid, because it affects the properties of charge of the surface of photocatalyst [20]. The evolution of the amount adsorbed at equilibrium on TiO₂ and ZnO in the absence of UV rays, and on the apparent rate constant of degradation as a function of pH is represented on the Figure 13. It follows from this Figure that the maximum rate of dye removal is observed in

an acid medium (pH = 3). Indeed, the point of zero charge (PCZ) is 6.8 for the TiO₂ and 8.9 for ZnO [21, 22]. For pH values of larger than PCZ, the catalyst surface is negatively charged according to the following electrochemical equilibrium:



At lower pH of the PH_{PZC}, the catalyst surface is positively charged:



It is clear that in acid medium the apparent rate constant decreases with the increase of pH for the dye on TiO₂ and ZnO. This is probably due to the absorption of the negatively charged molecule on the catalyst surface which bears an opposite charge. Then after the PZC the catalysts load negatively and we will have as consequence a repulsion between the surface and the groupings of negatively charged molecules. According to the figure it appears that the curves that represent the apparent rate constants of degradation and which decreases with the increase of pH have the same gait that those of the amount of dye molecules adsorbed to the adsorption equilibrium by gram. This result reinforces the idea that the step of adsorption is closely linked to the observed photocatalytic activity.

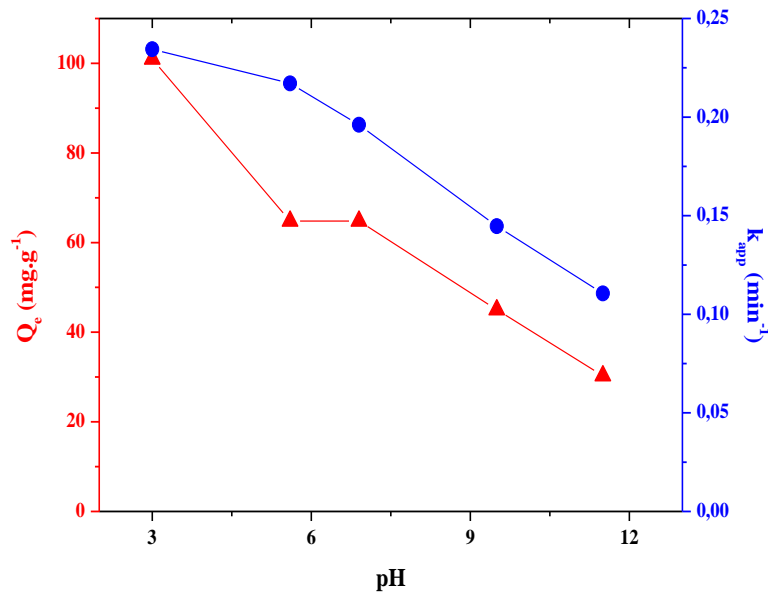


Figure 13 : Influence of pH on the amount of DR 80 adsorbed at equilibrium in the dark and on the apparent constant of degradation on TiO₂.

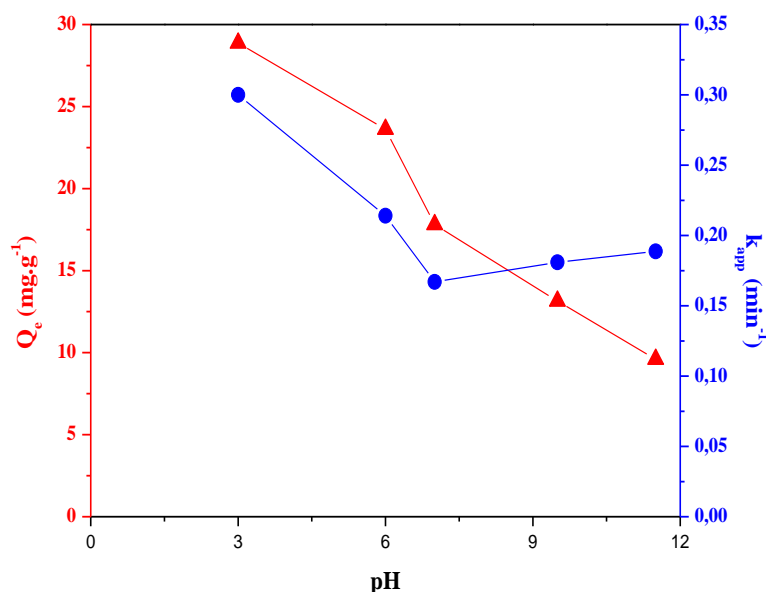


Figure 13 : Influence of pH on the amount of DR 80 adsorbed at equilibrium in the dark and on the apparent constant of degradation on ZnO.

CONCLUSION

The Photoelimination of dye DR 80 has been studied by means of two photocatalysts the most common, TiO₂ and ZnO. As well as the operational parameters such as the amount of catalyst, the initial concentration of dye and the initial pH of the reaction medium were also evaluated. The main conclusions drawn from this work are presented as follows:

- ✓ The adsorption is a critical step in the degradation by heterogeneous photocatalysis.
- ✓ The adsorption isotherm of dye DR 80 on TiO₂ is described satisfactorily by the Langmuir model while on ZnO and described by the Freundlich model.
- ✓ The kinetics of degradation is a function of the initial concentration of the dye.
- ✓ The reaction of photoelimination of the dye on the two catalysts follows well the model Langmuir-Hinshelwood.
- ✓ The pH is an essential parameter to take into consideration. The efficiency is very high at pH values strongly acid (pH = 3).

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