

## 17 $\alpha$ -ETHINYLESTRADIOL (EE2) PHOTOCATALYTIC DEGRADATION: ADSORPTION ISOTHERMS AND KINETICS

Diala Koumeir<sup>1,2</sup>, Chantal Guillard<sup>2</sup>, Sylvie Guittonneau<sup>1</sup> and Henri El Zakhem<sup>3\*</sup>

<sup>1</sup>University of Savoie – LCME 73376 Le Bourget du Lac cedex, France

<sup>2</sup>IRCELYON 2 Avenue Albert Einstein 69626 Villeurbanne cedex, France

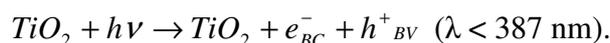
<sup>3</sup>University of Balamand, Faculty of Engineering, Chemical Engineering Department,  
POBox 33 Amioun, El Koura, Lebanon

E-mail: henri.elzakhem@balamand.edu.lb (\*Corresponding Author)

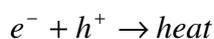
**Abstract:** In the present study, the degradation kinetics and mineralization of EE2 by the TiO<sub>2</sub> photocatalysis are examined in terms of UV absorbance of a wide range of initial EE2 concentration (mg.L<sup>-1</sup>) and photocatalyst loadings (0.5-24  $\mu$ mol.L<sup>-1</sup>) in a reactor system. Different parameters are studied and described in details, such as adsorption under dark and UV-A conditions, photolysis, kinetics of degradation, ions impact on the isotherm adsorption of EE2, as well as the photocatalytic degradation. EE2 adsorption isotherm follows the Langmuir model. The photocatalytic oxidation kinetic of EE2 is described by the Langmuir–Hinshelwood model, and it follows a kinetic of order one for concentrations that are below 6  $\mu$ mol.L<sup>-1</sup>, and then it reaches a plateau. For EE2, the coverage rates of the TiO<sub>2</sub> surface in the dark and under UV exposure are different. Total Organic Carbon (TOC) analysis shows a complete mineralization of intermediate products.

### 1. Introduction

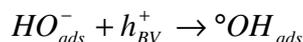
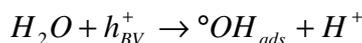
Heterogeneous photocatalysis using TiO<sub>2</sub> appears to be one of the most effective technologies [1-2] The TiO<sub>2</sub> photocatalyst is widely available, inexpensive, non-toxic, and shows a relatively high chemical stability. Additionally, the process can be carried out under ambient conditions and may lead to complete mineralization of organic carbon into CO<sub>2</sub>, water, and inorganic ions. In this process, UV light ( $\lambda \leq 387$  nm) is used to excite an electron from the TiO<sub>2</sub> [1] valence band to the conduction band to produce an electron-hole pair. The main reaction describing photocatalysis is:



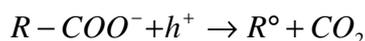
The average lifetime of an electron and a hole in a sample of TiO<sub>2</sub> are about 30 ps and 250 ns respectively, and their recombination is accompanied by heat [3-4]:



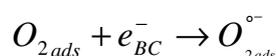
The hole  $h^+$  reacts with some species, such as water  $H_2O$  and anions  $HO^-$ , and they form hydroxyl radicals:



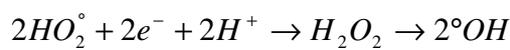
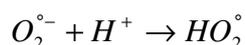
The hole  $h^+$  can also react by photo-Kolbe reaction with the carboxylate group  $COO^-$  of organic acids to form the radical  $R^\circ$ :



The electrons react with electron acceptors such as oxygen adsorbed on the catalyst surface to form superoxide radicals:



In the presence of adsorbed protons, the superoxide radical can lead to the formation of a hydroperoxide radical and hydrogen peroxide decomposed on the catalyst surface into hydroxyl radical under the action of radiation or by reaction with  $Ti^{3+}$  or  $O_2^{\circ-}$ :



Organic products  $RH$  adsorbed on the surface of the semiconductor  $TiO_2$  react with  ${}^\circ OH$  radicals, to form highly oxidizing radicals  $R^\circ$  which give through successive oxidation water and carbon dioxide.



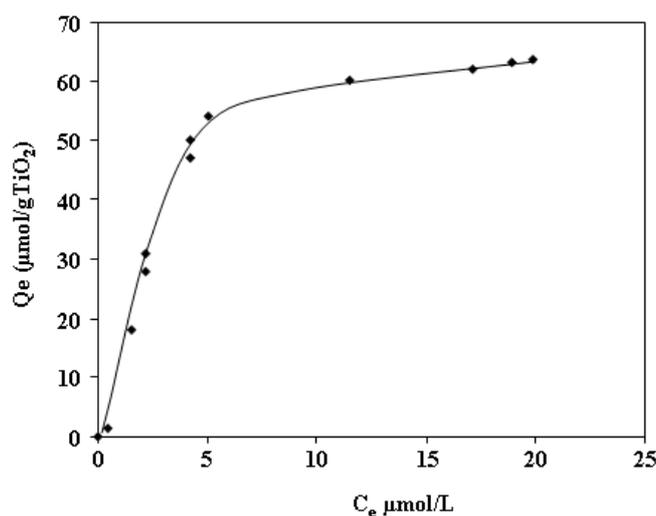
Thus, photocatalysis using  $TiO_2$  is successfully used for degradation of estrone, nitrogen compounds [4-5] pesticides [6-7-8-9], dyes [10-11-12], and microorganism which are difficult to be treated by biological methods [13]. EE2 was chosen in the present research to be degraded by heterogeneous photocatalysis using  $TiO_2$  Degussa P25 as photocatalyst. EE2 is widely used as an active ingredient in contraceptive pills [14]. The concentration of this steroid is constantly increasing in surface water ( $0.5-10 \text{ ng.L}^{-1}$ ) [15], which presents a real risk to wildlife (feminization of male fish and reduced reproduction). EE2 is one of the less polar estrogens (Log (P): 4.5), which tends to make it one of the most easily bioaccumulated molecule in biological organisms. In vivo tests have shown that it is potentially 11 to 27 times more toxic than the 17  $\beta$ -estradiol and estrone [16]. Other in vitro studies have shown the feminization of fish after exposure to  $0.1 \text{ ng.L}^{-1}$  of EE2 [17]. Ethinylestradiol is chosen

as a model molecule to illustrate the presence of an endocrine disruptor in waste water. Our work will therefore focus on a better understanding of the photocatalytic mechanism for the degradation of EE2 through the study of their adsorption kinetics under dark and UV conditions and through the evolution of their kinetics of photocatalytic degradation at different concentrations. The fate of carbon and nitrogen atoms will also be analyzed.

## 2. Results and Discussions

### 2.1 Adsorption

To determine the effect of the initial concentration of EE2 on the adsorption kinetics, different solutions of EE2 are maintained in the dark under stirring during 24h until equilibrium is reached.



**Figure 1 :** Adsorption isotherm of EE2 in  $\text{TiO}_2$  Degussa P25 (66 mg/L). Amounts of EE2 adsorbed per gram of  $\text{TiO}_2$  as a function of the equilibrium concentration  $C_e$ .

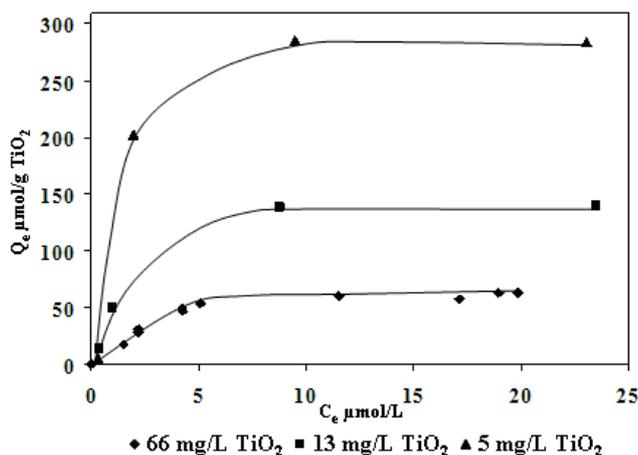
**Figure 1** represents the amounts ( $\mu\text{mol.g}^{-1}$ ) of EE2 adsorbed per gram of  $\text{TiO}_2$ . All results are represented as a function of the EE2 equilibrium concentration ( $C_e$ ). The results show that, in dark conditions, the amount of EE2 adsorbed on the  $\text{TiO}_2$  surface ( $Q_e$ ) increases with the equilibrium concentration until it reaches a plateau. The adsorption isotherm of EE2 on  $\text{TiO}_2$  P25 follows the Langmuir model. The adsorption constant and the maximum amount of EE2 adsorbed are given in **Table 1**.

**Table 1:** Model parameters for the Langmuir isotherm adsorption of EE2 on TiO<sub>2</sub> P25 ([TiO<sub>2</sub>] = 66 mg.L<sup>-1</sup>).

Langmuir Model	
$\frac{Q_e}{Q_{\max}} = \frac{KC_e}{1 + KC_e}$	
$Q_{\max}$ ( $\mu\text{mol/gTiO}_2$ )	$K$ (L/ $\mu\text{mol}$ )
70	0.22

## 2.2 TiO<sub>2</sub> P25 mass influence on adsorption

Three concentrations of TiO<sub>2</sub> P25 are studied 5, 13, and 66 mg.L<sup>-1</sup>. The selected catalyst concentrations are relatively low compared to concentrations usually studied in the literature, which are of the order of 1 g.L<sup>-1</sup>. It is revealed that for all concentrations of TiO<sub>2</sub> P25, adsorption isotherms represented in Figure 2 follow the Langmuir model.



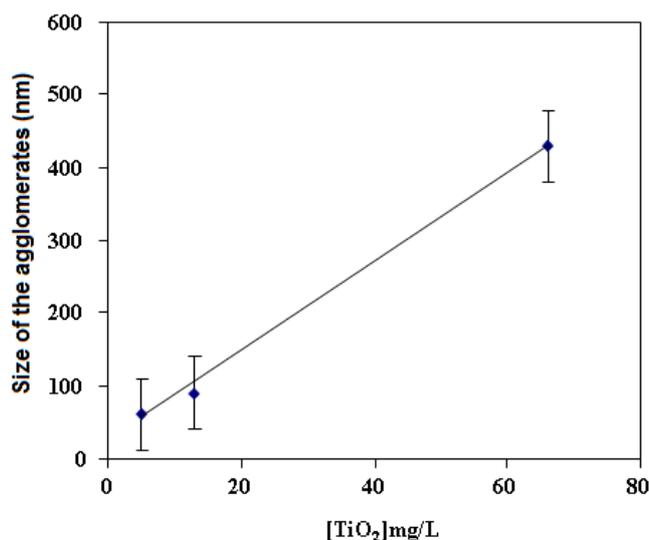
**Figure 2:** EE2 adsorption isotherm on different concentrations of TiO<sub>2</sub> P25.

For the same concentration of EE2, the amount adsorbed / g TiO<sub>2</sub> decreases when the concentration of TiO<sub>2</sub> increases. The characteristic parameters of the Langmuir model are calculated and given in **Table 2**.

**Table 2:** Model parameters for the Langmuir adsorption isotherm of EE2 for different concentrations of TiO<sub>2</sub> P25.

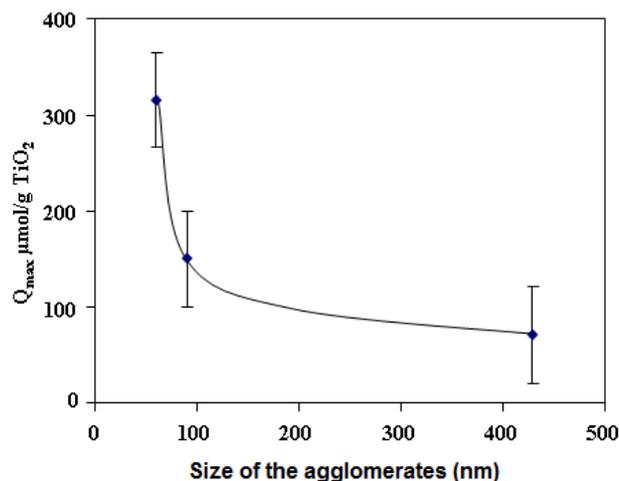
[TiO <sub>2</sub> P25]	Langmuir Model	
	$\frac{Q_e}{Q_{\max}} = \frac{KC_e}{1 + KC_e}$	
	$Q_{\max}$ ( $\mu\text{mol/gTiO}_2$ )	$K$ (L/ $\mu\text{mol}$ )
66	70	0.22
13	150	0.35
5	315	0.65

The maximum amount of adsorbed EE2 / g TiO<sub>2</sub> P25 and the adsorption constant decrease when the concentration of TiO<sub>2</sub> P25 increases, which suggests that the surface available for adsorption is smaller when the catalyst mass increases. Zhang *et al.* [18] in the study of the influence of the concentration of TiO<sub>2</sub> P25 on the adsorption of acetaminophen, found proportionality between the amount adsorbed and the concentration of TiO<sub>2</sub> knowing that the concentration range was from 0.25 to 1 g.L<sup>-1</sup> higher than the one of this study (some mg.L<sup>-1</sup>). The observed differences between our work and that of Zhang *et al.* may be explained by considering their higher concentrations of TiO<sub>2</sub>. We suggest that at high concentration of TiO<sub>2</sub>, the particles agglomerate and the available surface for the pollutants is reduced. Beyond a certain concentration, the size of the agglomerates remains constant. To test this hypothesis, the size of the agglomerates of TiO<sub>2</sub> P25 is measured at different concentrations of TiO<sub>2</sub> P25 (5, 13 and 66 mg.L<sup>-1</sup>). Agglomerates' size measurement is determined by photon correlation spectroscopy. The results are shown in **Figure 3**.



**Figure 3:** Size of the agglomerates versus the mass concentration of TiO<sub>2</sub> P25

The size of the agglomerates of TiO<sub>2</sub> P25 increases linearly with the concentration of TiO<sub>2</sub> P25 catalyst. This result proved our hypothesis about the formation of larger agglomerates by increasing the concentration of the catalyst. **Figure 4** shows that the amount of EE2 adsorbed decreases with the size of the agglomerates of TiO<sub>2</sub> P25.

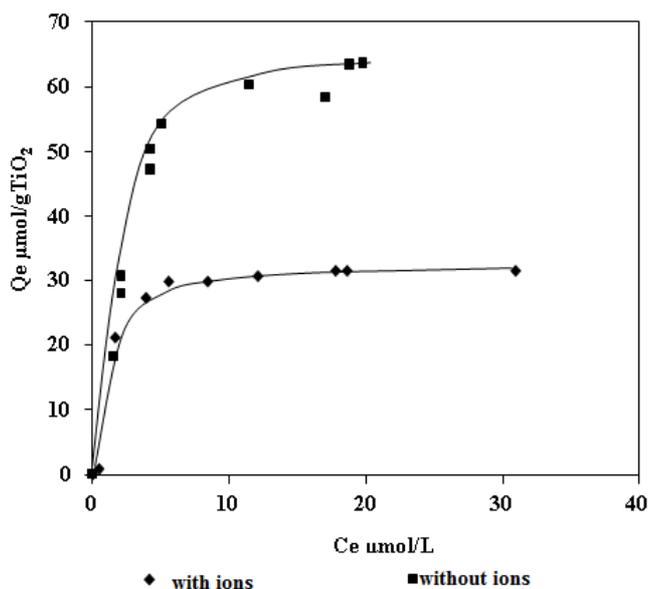


**Figure 3 :** Concentration of EE2 adsorbed versus agglomerates' particle size of  $\text{TiO}_2$  P25.

The results illustrated in **Figure 4** can be explained by the formation of agglomerates which reduce the available adsorption sites.

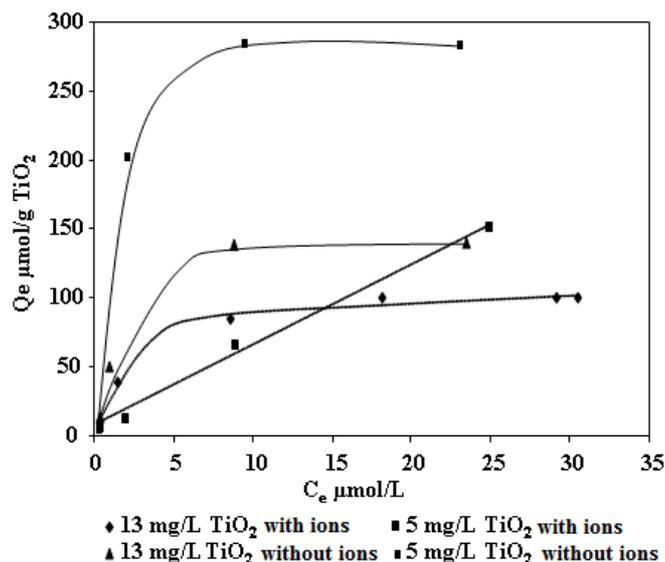
### 2.3 Influence of the presence of ions on the adsorption

In water treatment plants, ions are present in high concentrations. Therefore, it is important to study their impact on the isotherm adsorption of EE2, especially since this parameter has never been studied. **Figure 5** shows the adsorption isotherms of EE2 prepared in ultrapure water where the ionic strength ( $I$ ) is equal to  $7.4 \times 10^{-3} \text{ mol.L}^{-1}$ . The  $\text{TiO}_2$  P25 concentration is fixed to  $66 \text{ mg.L}^{-1}$ .



**Figure 5:** Adsorption isotherms of EE2 on  $\text{TiO}_2$  in the presence and in the absence of ions.  $[\text{TiO}_2] = 66 \text{ mg.L}^{-1}$

With or without ions, the isotherms obey Langmuir type. Concentration ( $C_e$ ) of EE2 required to saturate the available sites on the catalyst is slightly lower in the presence of ions, (about  $4 \mu\text{mol.L}^{-1}$ ). However, the maximum adsorbed amount of EE2 / g TiO<sub>2</sub> P25 is about two times lower in the presence of nitrate and sodium ions indicating that the number of sites available is lower. It is important to complete the study of the impact of ions on the isotherm adsorption by working with TiO<sub>2</sub>P25 concentrations of 13 and 5 mg.L<sup>-1</sup>. The results are shown in **Figure 6**.



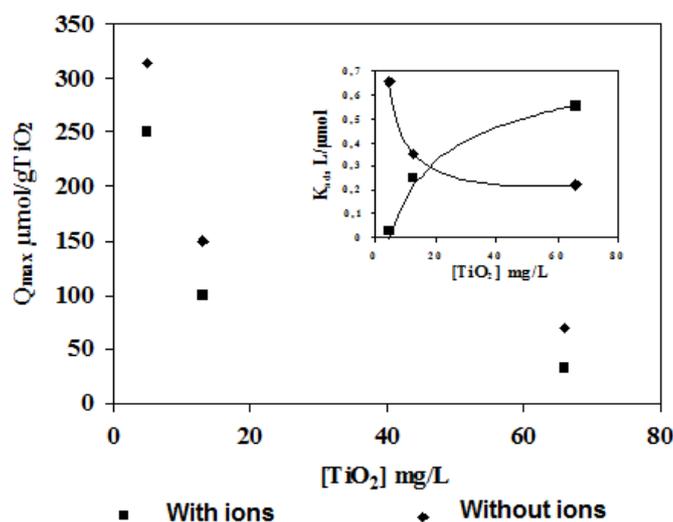
**Figure 6:** Adsorption isotherms of EE2 on TiO<sub>2</sub> P25 in the presence and in the absence of ions.  $[\text{TiO}_2] = 5 \text{ \& } 13 \text{ mg.L}^{-1}$

All adsorption isotherms follow the Langmuir model, except the adsorption isotherm obtained for  $5 \text{ mg.L}^{-1}$  of TiO<sub>2</sub> P25 in the presence of ions which is almost linear. This fact proves that the saturation zone described in Langmuir model does not apply in this case. The adsorption constants  $K$ , and the maximum quantities of adsorbable EE2 dissolved in pure water or in ions ( $\text{Na}^+$ ,  $\text{NO}_3^-$ ) containing solution are given in **Table 3**.

**Table 3:** Comparison of model parameters for the Langmuir adsorption isotherms of EE2 on TiO<sub>2</sub> P25 in the presence of ions (ionic strength  $I = 7.4 \times 10^{-3} \text{ mol.L}^{-1}$ ) and in the absence of ions (ionic strength  $I = 10^{-7} \text{ mol.L}^{-1}$ ), (\*) with respect to extrapolate the influence of ions on TiO<sub>2</sub> 13 and 66 mg.L<sup>-1</sup>.

Sample type	Concentration of TiO <sub>2</sub> (mg.L <sup>-1</sup> )	Langmuir Model	
		$Q_{\max}$ (μmol/gTiO <sub>2</sub> )	$K$ (L.μmol <sup>-1</sup> )
Water with (Na <sup>+</sup> ,NO <sub>3</sub> <sup>-</sup> )	13	100	0.25
Water with (Na <sup>+</sup> ,NO <sub>3</sub> <sup>-</sup> )	5	(250)*	(0.025)*
Ultrapure water	13	156	0.4
Ultrapure water	5	315	0.65

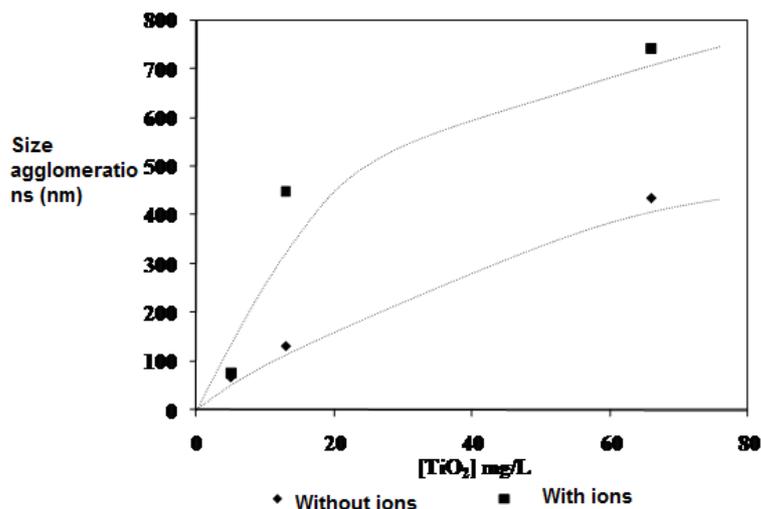
For all concentrations of TiO<sub>2</sub>, the presence of ions in the initial solution of EE2 affects adsorption by reducing the quantities adsorbed. **Figure 7** represents the maximum amount of adsorbed EE2 / g TiO<sub>2</sub> P25 in the presence and in the absence of ions.



**Figure 7:** Maximum amount of adsorbed EE2 / gram of TiO<sub>2</sub> versus TiO<sub>2</sub> concentration, in the presence and in the absence of ions.

From **Figure 7**, we can extrapolate the value of  $Q_{\max}$  in the presence of ions at a TiO<sub>2</sub> P25 concentration of 5 mg.L<sup>-1</sup>. It is 250 μmol/g TiO<sub>2</sub> with  $K = 0.025 \text{ L.mol}^{-1}$ . This means that unlike the behavior of  $K$  in pure water (decreasing then reaching a plateau), in the presence of

ions, adsorption constant increases before reaching a plateau (insert in **Figure 7**). These results indicate that with the presence of ions, the number of adsorption sites has changed. This decrease of the number of adsorption sites can be explained either by considering a competition between the molecules of EE2 and the ions, or by considering a change in the size of the agglomerates. To test this latter hypothesis, the size of the clusters is measured and compared with that measured in the absence of ions (**Figure 8**).

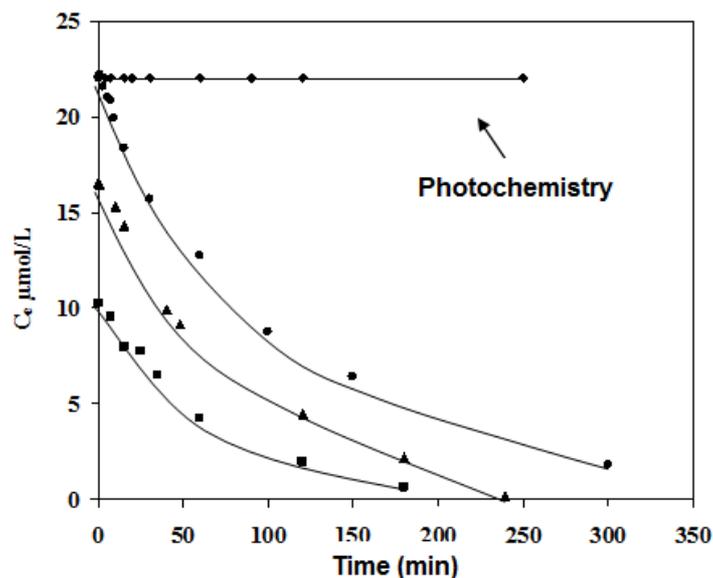


**Figure 8:** Size of the agglomerates of TiO<sub>2</sub> versus TiO<sub>2</sub> concentration in the presence and in the absence of ions.

At 5 mg.L<sup>-1</sup> of TiO<sub>2</sub>, the presence or the absence of ions seems to have no impact on the size of the agglomerates of TiO<sub>2</sub>. However, given the limitations of the technique, it is difficult to conclude. At 13 and 66 mg.L<sup>-1</sup> of TiO<sub>2</sub> P25, the presence of ions in the solution increases drastically the size of the agglomerates of TiO<sub>2</sub>. TiO<sub>2</sub> particles clump together to form aggregates which are larger in the presence of ions. In fact, ions form micelles with water which leads to the formation of larger agglomerates with TiO<sub>2</sub>. Consequently, the adsorption sites on the catalyst surface are reduced.

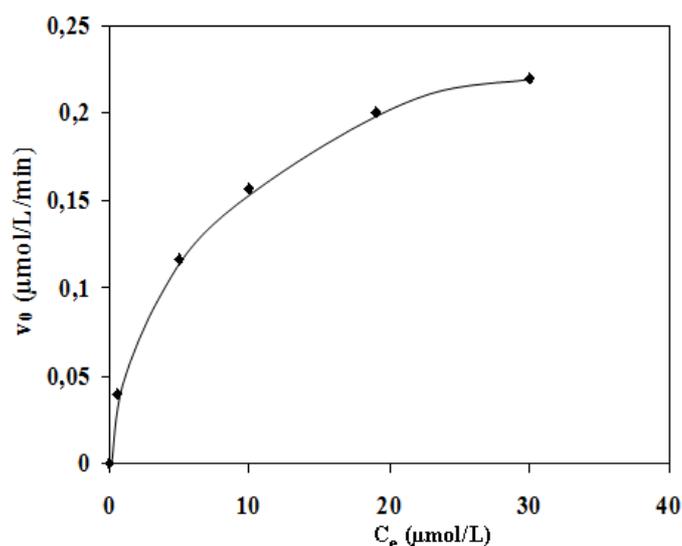
#### 2.4 Degradation of EE2 in the presence of TiO<sub>2</sub> P25

The photocatalytic degradation of EE2 is studied at different concentrations of EE2 ranging from 0.34 to 22  $\mu\text{mol.L}^{-1}$  in the presence of TiO<sub>2</sub> P25 concentration of 66 mg.L<sup>-1</sup>, under UV irradiation. **Figure 9** shows both the photochemical degradation of EE2 without photocatalyst and the photocatalysis degradation of three concentrations of EE2 (10, 16 and 22  $\mu\text{mol.L}^{-1}$ ) in function of irradiation time and in the presence of 66 mg.L<sup>-1</sup> of TiO<sub>2</sub> P25.



**Figure 9:** Degradation kinetics of different concentrations of EE2 (10  $\mu\text{mol}\cdot\text{L}^{-1}$ , 16  $\mu\text{mol}\cdot\text{L}^{-1}$ , and 22  $\mu\text{mol}\cdot\text{L}^{-1}$ ) in the presence of 66  $\text{mg}\cdot\text{L}^{-1}$  of  $\text{TiO}_2$  P25 ( $\text{pH} = 7.5$ ,  $V = 750$  mL,  $\Phi = 2.2$   $\text{mW}/\text{cm}^2$ ).

In the presence of photocatalyst, the initial concentrations of EE2 decrease exponentially with time. In the absence of  $\text{TiO}_2$ , no degradation is observed, confirming that this degradation is due to the photocatalytic process. The initial rates of degradation of 17  $\alpha$ -ethinylestradiol ( $v_0$ ), determined from **Figure 9**, are plotted versus the concentration of EE2 remaining in solution after adsorption ( $C_e$ ) (**Figure 10**).



**Figure 10:** Evolution of the initial rate of degradation of EE2 in the presence of 66  $\text{mg}\cdot\text{L}^{-1}$  of  $\text{TiO}_2$  P25 ( $\text{pH} = 7.5$ ,  $\Phi = 2.2$   $\text{mW}/\text{cm}^2$ ).

The initial rate increases linearly with the concentration of EE2 ( $C_e$ ). For low concentrations, the reaction is of order 1 ( $v_0 = k' = k.K$ ). At high concentrations, the degradation rate increases to a maximum (reaction of order 0). The model of Langmuir-Hinshelwood (LH) is frequently used to model the photocatalytic reactions. The reaction rate ( $v$ ) can be expressed by the following equation:

$$v = k\theta = \frac{k.K.C_e}{1 + K.C_e}$$

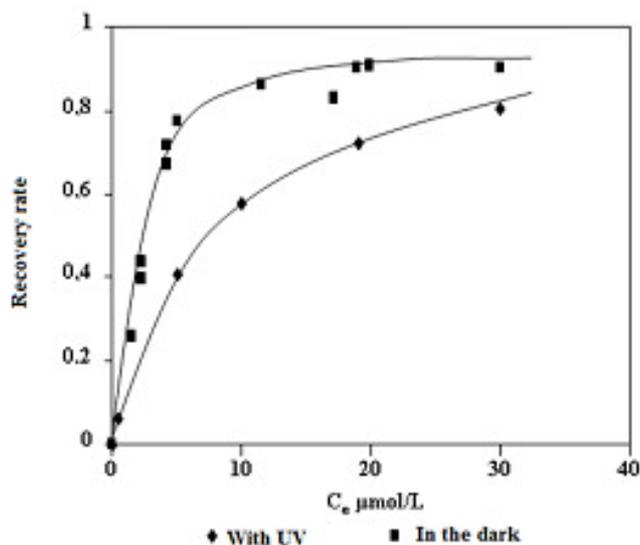
where:

$k$  is the kinetics constant of degradation of EE2 ( $\mu\text{mol/L/min}$ )

$\theta$  is the fraction of active sites on the surface of  $\text{TiO}_2$  covered with EE2, it is related to the concentration of EE2 ( $C_e$ ) according to the Langmuir equation:

$$\theta = \frac{K.C_e}{1 + K.C_e}$$

$K$  is the adsorption constant of EE2 on the surface of  $\text{TiO}_2$  ( $\text{L}/\mu\text{mol}$ ). The kinetics and adsorption constants ( $k, K$ ) are determined using the method of least squares. The values of  $k$  and  $K$  are respectively  $0.24 \mu\text{mol/L/min}$  and  $0.13 \text{L}/\mu\text{mol}$ . Assuming that  $v = k\theta$ , **Figure 11** shows the variation of the recovery rate in function of the concentration of EE2 under UV and in the dark.



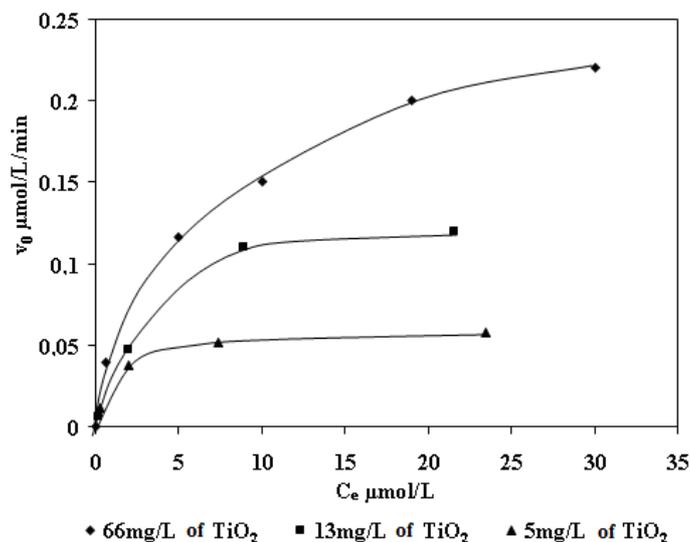
**Figure 11:** Evolution of recovery rate in function of the concentration of EE2 at equilibrium ( $[\text{TiO}_2] = 66 \text{ mg/L}$ ) in the absence of ions.

The recovery rate  $\theta$  increases with the concentration ( $C_e$ ) until it reaches a saturation plateau from about  $5 \mu\text{mol/L}$  EE2. The evolution of the recovery rate observed under UV is not the

same as that observed in the dark. Under UV, the recovery rate is reached less rapidly. This implies that the adsorption sites are not all active sites. Several hypotheses have been advanced by research groups: there could be a photo-adsorption [19], or photodegradation of the reaction could take place not only on the surface but also in solution [20], or there could be insufficient adsorption sites to initiate the reaction [21], or a change of surface electronic properties of  $\text{TiO}_2$  could change the distribution of adsorption sites [22].

### 2.5 Influence of the concentration of $\text{TiO}_2$ P25 on the kinetics

The concentration of  $\text{TiO}_2$  in suspension is a parameter that can influence the kinetics of photocatalytic degradation. To better understand the influence of this parameter, different concentrations of  $\text{TiO}_2$  are tested for the photocatalytic degradation of  $17\alpha$ -ethinylestradiol. The values of the initial rate of EE2 degradation are presented against the initial concentration at different concentrations of  $\text{TiO}_2$  P25 in **Figure 12**.



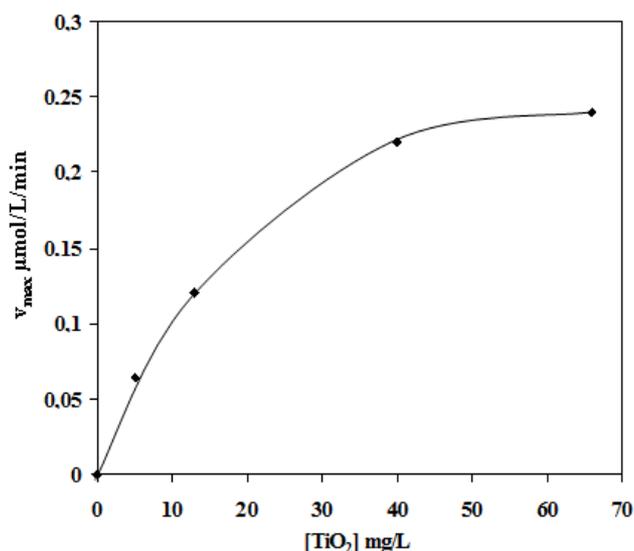
**Figure 12:** Changes in the rate of degradation of EE2 depending on the concentration of EE2 and various concentrations of  $\text{TiO}_2$  P25.

For all catalyst concentrations, it was proved that initial rates of degradation follow the Langmuir-Hinshelwood model. The initial rates of degradation increase linearly with the concentration of EE2 at equilibrium then reach a plateau. The characteristic parameters of this model are given in **Table 4**.

**Table 4:** Parameters of Langmuir and Langmuir-Hinshelwood for different concentrations of  $\text{TiO}_2$  P25.

$[\text{TiO}_2]$ P25 mg/L	$k$ ( $\mu\text{mol/L}/\text{min}$ )	$K$ ( $\text{L}/\mu\text{mol}$ )	$K$ ( $\text{L}/\mu\text{mol}$ ) (calculated from adsorption study)
66	0.24	0.13	0.22
13	0.13	0.27	0.35
5	0.06	0.5	0.65

For all  $\text{TiO}_2$  concentrations, the adsorption constants under UV are always lower than those obtained in the dark. This phenomenon has been described by several authors [19-20-21-22]. The constant of degradation rate increases with the concentration of the catalyst  $\text{TiO}_2$  P25. **Figure 13** shows the maximum rates of degradation that can be reached for each concentration of the catalyst  $\text{TiO}_2$  P25.

**Figure 13:** Influence of catalyst concentration on the speed of photocatalytic degradation of EE2 ( $C_e = 19.2 \mu\text{mol/L}$ )

Maximum rates of EE2 degradation increase with the concentration of the catalyst  $\text{TiO}_2$  P25 until they reach a plateau. Above a certain concentration of  $\text{TiO}_2$  P25, the photocatalytic degradation rate becomes independent of the concentration of the catalyst. This limit depends on the geometry of the photoreactor and its conditions (i.e. intensity of radiation). Under our experimental conditions 40 mg/L  $\text{TiO}_2$  is the optimum concentration  $\text{TiO}_2$  for which all the catalyst particles are fully occupied. For larger amounts of catalyst, an excess of particles is present, masking a portion of the photosensitive surface. To understand the relationship between the photocatalytic activity of EE2 and the UV range used during the irradiation, the yield efficiency of photons emitted during irradiation is considered. Previously, to monitor

the kinetics of photodegradation of EE2, the irradiated surface had to be reduced by placing a cache around the lamp. The flow of irradiation is  $2.2 \text{ mW.cm}^{-2}$  at 365 nm. The yield of photons emitted by UV irradiation during the degradation reaction with EE2 to 365 nm is calculated according to the following relationships:

- Energy of luminous flux  $E = \frac{hc}{\lambda}$

Planck's constant  $h = 6.62 \times 10^{-34} \text{ J.s}$ , the speed of light,  $c = 3.10^8 \text{ m.s}^{-1}$  and the wavelength of 365 nm radiation. We obtain:  $E = 5.44 \times 10^{-19} \text{ J.photons}^{-1}$ .

- Number of photons at 365 nm:  $\varphi = \left(\frac{\Phi}{E}\right) \times S$

With the luminous flux  $\Phi$  in  $\text{W.cm}^{-2}$ , energy flow  $E$  in  $\text{J.photons}^{-1}$ , and the surface irradiated  $S$  is equal to  $14.13 \text{ cm}^2$ . The total number of photons in this case is equal to  $5.71 \times 10^{16} \text{ photons.s}^{-1}$ .

- Quantity of moles of photons  $\varphi_n = \frac{\varphi}{N_A}$

- With Avogadro's number  $N_A$ ,  $6.023 \times 10^{23} \text{ mol}^{-1}$  and the number of photons  $\varphi$  in  $\text{s}^{-1}$ .  $\varphi_n$  is obtained =  $9.4 \times 10^{-8} \text{ mol.photons.s}^{-1}$ .

Finally, the performance efficiency of the photons  $\rho$  emitted during the degradation reaction of ethinyl estradiol is determined at 365 nm, using the following equation:

- Performance efficiency of emitted photons

$$\rho = \frac{v}{\varphi_n} = \frac{\text{mole of EE2 degraded / s}}{\text{mole of photon emitted / s}}$$

The results are shown in **Table 5**.

**Table 5:** Performance efficiency of the emitted photons with  $\text{TiO}_2$  P25.

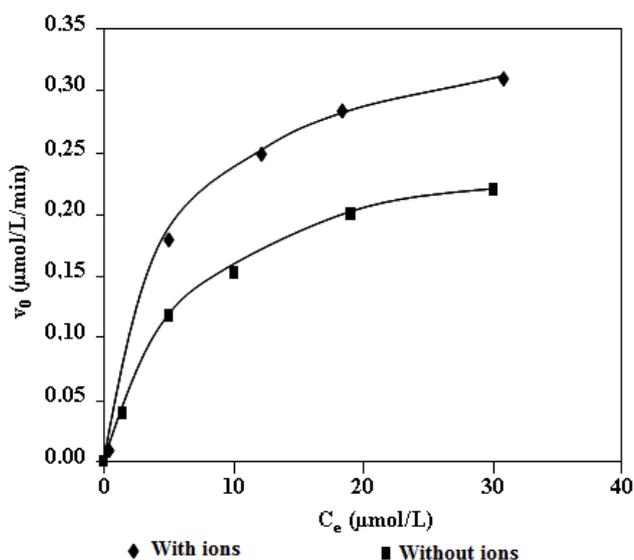
$[\text{TiO}_2]$ mg/L	$\text{vx}10^{-9} \text{ mol.s}^{-1}$	$\rho$
66	3	0.031 (3.1%)
40	2.9	0.03 (3%)
13	1.6	0.017 (1.7%)
5	0.75	0.0079 (0.8%)

The calculation of performance efficiency of the emitted photons evidences that the photocatalytic efficiency increases with the concentration of the catalyst. With 66 mg/L of

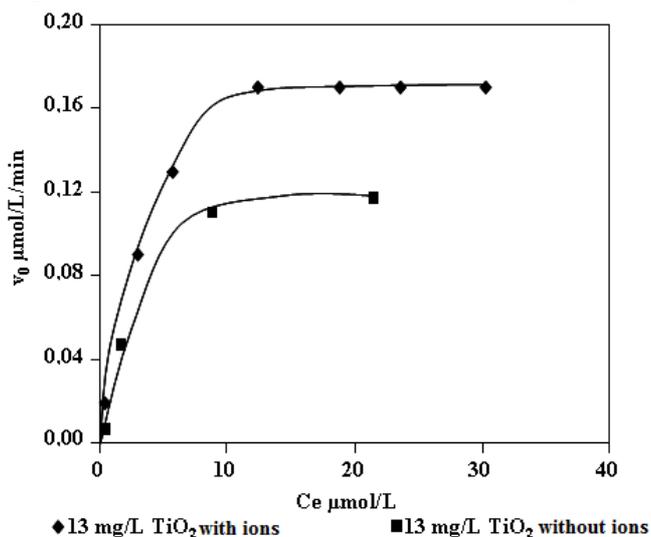
TiO<sub>2</sub>, efficiency is about 2 times and 4 times greater than that with 13mg/L and 5mg/L of TiO<sub>2</sub> respectively.

## 2. 6 Influence of the presence of ions on the degradation

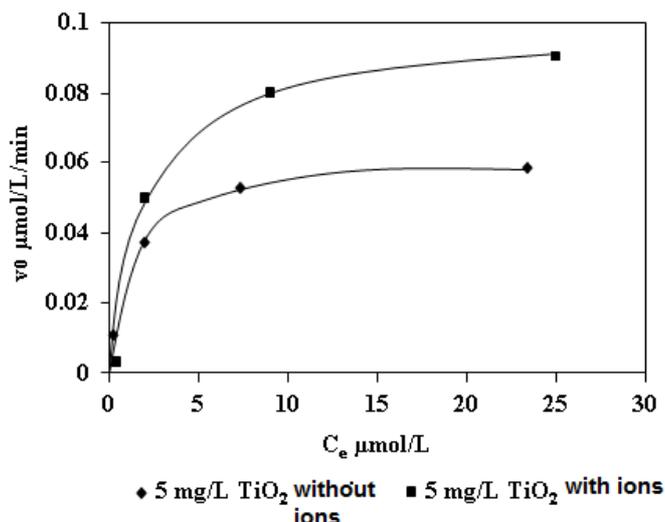
In our study, the effect of Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup> is observed on the rate of degradation of EE2. This type of study, to our knowledge, not been performed on this molecule. The evolution of the initial rates, in the ions presence (Ionic strength  $I = 7.4 \times 10^{-3}$  mol/L) and absence (Ionic strength  $I = 10^{-7}$  mol/L), is plotted against the EE2 concentration with different TiO<sub>2</sub> P25 concentrations (Figure 14, Figure 15, and Figure 16).



**Figure 14:** Evolution of the degradation rate  $v_0$  versus EE2 concentration in the ions' presence and absence, with  $[\text{TiO}_2] = 66\text{mg/L}$ .



**Figure 15:** Evolution of the degradation rate  $v_0$  versus EE2 concentration in the ions' presence and absence, with  $[\text{TiO}_2] = 13\text{mg/L}$ .



**Figure 16:** Evolution of the degradation rate  $v_0$  versus EE2 concentration in the ions' presence and absence, with  $[\text{TiO}_2] = 5 \text{ mg/L}$ .

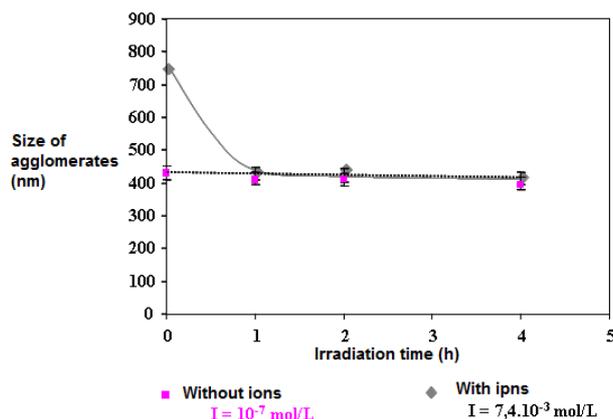
With or without ions, the evolution of the degradation rate follows the Langmuir-Hinshelwood model. The saturation plateau described by this model and the initial rate of degradation are increasingly important in the presence of ions. **Table 6** represents the characteristic parameters of the Langmuir-Hinshelwood models for ultrapure water and water containing ions for the various concentrations of  $\text{TiO}_2$  P25.

**Table 6:** Langmuir-Hinshelwood parameters for different concentrations of  $\text{TiO}_2$  P25 in the presence of ions (ionic strength  $I = 7.4 \times 10^{-3} \text{ mol/L}$ ) and in the absence of ions (ionic strength  $I = 10^{-7} \text{ mol/L}$ ).

$[\text{TiO}_2]$ mg/L	$k$ ( $\mu\text{mol/L}/\text{min}$ )		$K$ ( $\text{L}/\mu\text{mol}$ )		$K$ ( $\text{L}/\mu\text{mol}$ ) (calculated from the adsorption study)	
	Water with ions	Ultrapure water	Water with ions	Ultrapure water	Water with ions	Ultrapure water
66	0.34	0.24	0.18	0.13	0.55	0.22
13	0.17	0.13	0.29	0.27	0.25	0.35
5	0.09	0.06	0.41	0.5	0.025	0.65

**Table 6** shows that the adsorption constants obtained under UV are different from those determined in the dark. This lack of correlation has been reported numerous times. In the presence of ions, the UV adsorption constant is relatively close to that obtained in ultrapure water. The presence of ions ( $\text{Na}^+$ ,  $\text{NO}_3^-$ ) in the initial solution of EE2 plays a complex role in the photodegradation of the molecule. They induce an adverse effect on the adsorption of the

molecule to the catalyst surface, explained by the increase in the size of agglomerates of TiO<sub>2</sub> P25. For a concentration of TiO<sub>2</sub> of 66 mg/L, the size of agglomerate is almost double in the presence of ions. However, unlike the adsorption in the presence of ions, the rate of degradation of EE2 is increased. This leads us to assume that UV irradiation reduces the surface of TiO<sub>2</sub> by reducing the size of its agglomerates. The size of TiO<sub>2</sub> particles is measured in function of irradiation time **Figure 17**.



**Figure 17:** Measurement of the size of the TiO<sub>2</sub> particles in function of irradiation time.

In the absence of ions, UV irradiation has no effect on the size of the agglomerates of TiO<sub>2</sub> P25. Contrarily, in the presence of ions, UV irradiation decreased their sizes. This may confirm the hypothesis suggested above. In the literature, the effect of ions on the photodegradation is debatable. Most studies show an inhibitory effect of ions on the photodegradation [23-24]. The photodegradation of methylene blue shows an inhibitory effect of ions on the photodegradation of the molecule. Several hypotheses suggested that the presence of these ions: (i) increases the rate of recombination  $e^-/h^+$  [25-26-27-28], (ii) traps the hydroxyl radicals [29], (iii) creates competitive adsorption between the ions and the pollutant on the surface of the catalyst [30]. However, Zhang *et al.* [30] showed that the photodegradation of reactive brilliant orange is enhanced in the presence of nitrate ions. They suggest the formation of hydroxyl radicals produced from the photolysis of nitrate ions in the solution at  $\lambda = 302$  nm.

### 3. Experimental

#### 3.1 Materials

The 17  $\alpha$ -ethinylestradiol (EE2) is purchased from Sigma Aldrich and used as received without purification. Solutions are prepared under different concentrations in Ultra-Pure

water from Elgastat UHQ PS Elga LabWater. The 17  $\alpha$ -ethinylestradiol (EE2) is in the form of a white crystalline solid, soluble in most organic solvents.

The photocatalyst used is Titanium dioxide Degussa P-25. Its specific surface is between 50 and 55 m<sup>2</sup>.g<sup>-1</sup> with particle size of 30 nm.

### 3.2 Adsorption experiments

750 mL of EE2 with different initial concentrations are placed in the reactor at neutral pH. It is then placed for 24 hours under magnetic stirring in the dark and in the presence of a given concentration of TiO<sub>2</sub>. This time is necessary to reach the equilibrium between adsorption and desorption. Three concentrations of TiO<sub>2</sub> P25 are studied: 5, 13, and 66 mg.L<sup>-1</sup>. To determine the quantities of EE2 adsorbed on TiO<sub>2</sub>, samples are filtered using a 0.45  $\mu$ m Millipore filters and analyzed on HPLC.

### 3.3. Photocatalytic experiments

The photoreaction is carried out in a Pyrex cylindrical reactor of a volume of 1 liter. The radiant flux is provided by a high-pressure mercury lamp Philips HPK 125 W which provides maximum energy at 365 nm. An optical filter is installed to cut-off any radiation of wavelength below 300 nm. A circulating water system is installed to avoid heating of the solution subjected to UV irradiation. The radiant flux is measured with a VLX-3W radiometer with a CX-365 detector (UV-A). A value of 2.2 mW/cm<sup>2</sup> is found corresponding to about 5.71x10<sup>16</sup> photons.s<sup>-1</sup>.

### 3.4. Analyses

The concentrations of EE2 remaining after the adsorption and during the photocatalytic degradation process are determined using a high performance liquid chromatography in reverse phase. C18 (125x4 mm) (Interchrom) column is used with Water/ACN (50/50) as eluent at a flow rate of 0.8 mL.min<sup>-1</sup>. HPLC is coupled with UV-vis detector (Varian prostar 325 UV-Vis  $\lambda = 220$  nm). Total Organic Carbon (TOC) is determined with a Shimadzu model TOC-Control V provided with an autosampler. Agglomerate size of TiO<sub>2</sub> P25 at different concentrations of TiO<sub>2</sub> P25 (5, 13 and 66 mg.L<sup>-1</sup>) is determined by photon correlation spectroscopy.

## 4. Conclusions

17- $\alpha$ -Ethinylestradiol is degraded by photocatalysis in the presence of TiO<sub>2</sub> P25 under UV irradiation ( $\lambda = 365$  nm). The optimal concentration of the catalyst to degrade ethinylestradiol is less than 60 mg/L. This concentration is relatively low compared to that found in the literature (1 g/L) confirming the effectiveness of our method to eliminate this kind of

endocrine disruptor. EE2 degradation is modeled satisfactorily by the models of Langmuir and Langmuir-Hinshelwood. However, the adsorption constants calculated by the model LH do not correspond to those calculated by the Langmuir model. This fact suggests that the active sites are not only the adsorption sites in the dark, and that the Langmuir-Hinshelwood model is not applicable. Unlike the adsorption, the increase of the ionic strength  $I$  of the solution facilitates the photodegradation of EE2.

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