

# Mathematical modeling of drug Removal by using TiO<sub>2</sub> as Photo Catalysis

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**Abstract:** *The occurrence, fate and effects of Pharmaceuticals compounds (PhCs) in the environmental system have been attracted special attention recently as new emerging contaminants due to their potential impact on humans, animals and microorganisms even at low concentrations. Conventional wastewater treatment technologies, including biological, thermal and physical treatments, are found to be insufficient for removal of many pharmaceuticals residues from wastewater, due to their low biodegradability and high chemical stability. Advanced oxidation processes (AOPs), are one of the most promising treatment technologies for elimination of such relentless compounds. In developing and further understanding of photo catalytic processes, there are two major approaches: The first one is to build up laboratory / pilot scale process, and the second one is to use commercial software. Unfortunately, in the last case of the drug removal by TiO<sub>2</sub> photo catalytic process there is no commercial software able to predict the behavior of the drug removing by using the photo catalytic process.*

*In order to start building software that can describe the photo catalytic process a mathematical model in this study is proposed and illustrated.*

*Mathematical modeling can be defined as a tool that uses mathematical language to describe a physical system, which is not only used in the natural sciences and engineering disciplines but also in the social sciences. So mathematical modeling is: "a representation of the essential aspects of an existing system (or a system to be constructed) which presents knowledge of that system in usable form". Based on these definitions the main objective of the mathematical modeling is to describe (mathematically) the different aspects of the real world, the interactions, and the dynamics.*

**Keywords:** *Photo catalytic, Mathematical modeling, TiO<sub>2</sub>, Pharmaceuticals removal*

## 1. Introduction

Conventional sewage treatment processes (STPs) are not efficient to remove recalcitrant compounds (pharmaceuticals and pesticides). Which have been detected at very low concentrations in surface waters and in drinking water [1]-[5].

Pharmaceuticals residues and their metabolites can induce toxic effects, as in the cases of antibiotic and steroids that cause resistance in natural bacterial populations or endocrine disruption effects and in aquatic environment the organisms exhibiting the same enzyme receptors as humans could experience similar pharmacodynamic effects [6]-[7].

AOPs have been applied to remove recalcitrant organic contaminants from the aquatic environment. Sulaiman et al. (2014a)[8] used the membrane separation technology which includes sequential elements Ultra-filtration (UF), Activated carbon column (AC) and Reverse osmosis (RO), and adsorption technology using surface modified composite materials micelle (ODTMA)-clay complex and activated carbon for removing Dexamethasone sodium phosphate and Diazepam [8]-[9]. Nevertheless, these technologies are considering only phase-transfer technologies and expensive[9]-[10].

In this research, our methodology was focusing on providing an economical treatment method, for that, all experiments was performed under solar light through introduce a treatment

technology leads for complete destruction and mineralization of most organic pollutants traces that may present in environment. To this end, Advanced oxidation processes (AOPs) have been proposed as an alternative purification techniques. Among those types of AOPs employed, heterogeneous photo-catalysis with TiO<sub>2</sub> semiconductors was applied in this research towards removing pollutants such as pharmaceuticals and pesticides, TiO<sub>2</sub> was generally demonstrated to be the most active semi-conducting materials, since it is strong resistance to chemical- and photo-corrosion, safety and low cost. On the other hand, It can use natural (solar light) [Wu, 2008]. Hence, the hypothesis that was tested in this research was that photocatalytic degradation with either TiO<sub>2</sub> powder, or immobilized on different stationary supports can efficiently remove trace levels of both pharmaceuticals and pesticides or other recalcitrant organic compounds that may exist in wastewater treatment plant effluents and in drinking water sources.

Mathematical modeling, that is a set of algebraic, ordinary and partial differential equations used to describe the steady state and in general the dynamic behavior of the system under consideration, plays an important role also in design and in understanding different processes [11]-[12].

The increasing importance of the mathematical modeling expands the research abilities to transfer mathematical

symbols and equations into a concrete reality that concerned with both sides of the artificial and natural world.

## 2. Factors affecting solar photo catalysis

Reaction rate considered one of the most important methods that can be used to describe the mechanisms of reaction.

A common way to express the reaction rate is to use the power law:

$$r = \frac{dc}{dt} = kC^n \quad (1)$$

where  $k$  is the rate constant and  $n$  is the order of the reaction and  $C$  is the concentration of reactants. In general, first and second order models are more common [13].

For the first-order reactions the rate depends on the concentration of the reactants with a unit of ( $s^{-1}$ ). while for the second-order reactions the rate depends on the concentration of the reactants squared, and rate constant has the unit of ( $M s^{-1}$ ) [13].

All chemical reactions proceed through different steps with the formation of intermediates. These reactions are very complexes because different parameters are involved: for this reason it is impossible to apply a general law especially in the pollutant degradation field.

In this research the efficiency of photo-catalysis on the removal of some pharmaceuticals dissolved in liquid solution was studied and evaluated.

Different factors were found to affect the degradation rate: light intensity, oxygen concentration, temperature, pH,

The model is based on four important assumptions [16]:

1. The entire catalyst surface has the same activity for adsorption (energetically uniform).
2. There is no interaction between adsorbed molecules and the amount adsorbed does not affects the adsorption rate.
3. All the adsorption occurs by the same mechanism.
4. The extent of adsorption is less than one complete monomolecular layer.

### 2.1. Effect of Light Intensity on Reaction Rate

Since light intensity determines the rate of generation of the photo-induced electron and holes in the catalyst, Egerton and King 2002 [17] were able to show that the reaction rate should be directly proportional to intensity at low fluxes and proportional to the square root of intensity at relatively high flux levels. When the depletion of the surface reactant is included, the dependence of reaction rate on light intensity undergoes transition from linearity to a non-linear dependence ( $I^{1/2}$ ) as intensity increases.

It appears that at high light intensity the recombination of the electron hole pair is enhanced while at low fluxes organic oxidation can compete with recombination.[17]-[19]. Further, the rate becomes independent of light intensity at higher fluxes

pollutant contents, relation among particle size, reactor diameter and  $TiO_2$  concentration, Contact time and surface area.

These factors were investigated and the kinetic parameters derived from the corresponding experimental data.

The kinetic data evaluated by applying different methods varies from simple data plots and evaluation of the kinetic data using the concept of intercept and slope up to complex analysis methods like least square refinement and Levenberg-Marquardt [14] passing through the application of pseudo first order reaction.

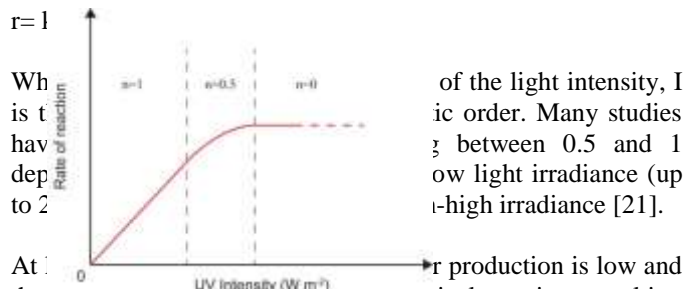
Heterogeneous catalytic reactions are considered to be a very important branch of chemistry and pharmaceutical studies due to their relevance in many different industrial applications (from oil to pharmaceutical industries). Catalytic reactions usually occur between active sited and molecules adsorbed on the surface of the catalyst.

Langmuir's works at the beginning of twentieth century has a major contribution to the understanding of the adsorption-desorption equilibrium phenomena, which includes the formulation of a suitable reaction rate law for the catalytic surface reactions [15].

Langmuir developed a model that is able to describe the equilibrium relation between the concentration of adsorbent in the gas (or liquid) and the amount adsorbed on the surface.

and the expected rate-limiting factor becomes the mass transfer [20].

Being the photo-catalytic process initiated starting by the absorption of a light photon, most investigations have studied the effect of the absorbed light intensity [21]. It is well known that the photon flux can be correlated to the reaction rate by,

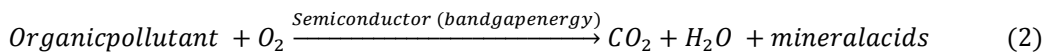


At low light intensity, the rate of reaction is low and they are readily consumed by the chemical reactions resulting in a first order regime. At medium-high light intensity the rate of excitant pairs formation is higher than their consumption resulting in a faster recombination of the charges and in a half order regime as indicated in Figure 1.

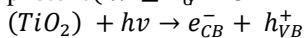
Some researchers also reported a zero order but it has been demonstrated that the plateau reached on the graph between light intensity and reaction rate is a mass transfer limitation in disguise rather than an extreme rate of charge recombination. This condition is encountered in experiments where the concentration of pollutants is very low (below ppm) and the light intensity is quite high. In these cases, it was demonstrated that an increase in the light intensity does not have any effect on the reaction rate because the reaction is happening under mass transfer control conditions (very low pollutant concentration) and not under reaction control [23]. The oxidation of organics is directly proportional to the concentration of positively charged holes formed by absorption of UV radiation. [24] The concentration of photo-generated holes is determined by recombination and reaction with organic compounds. Therefore, the reaction rate of  $h^+$  can be expressed in the following manner:

$$\frac{d[h^+]}{dt} = -k_3 [h^+] - k_{-3} [e^-][h^+] - k_4 [h^+] \theta_D + k_2 \sqrt{I} + g \quad (6)$$

where  $[h^+]$  is the density ( $\text{cm}^{-3}$ ) of valence band holes in the semiconductor particle;  $g$  represents the generation rate of photo-induced  $e^- - h^+$  pairs ( $\text{cm}^{-3} \text{s}^{-1}$ ), which can be calculated from the flux of the incident light ( $I$ ), absorption coefficient of the system, and the density of the semiconductor material.  $k_3 k_4$  are the rate of hole transfer ( $\text{s}^{-1}$ ); and  $k^{-3} (\text{s}^{-1})$  is the



The concentration of oxygen also affects the reaction rate but it seems that the difference between using air ( $p\text{O}_2 = 0.21 \text{ atm}$ ) It's well establish that by irradiation of an aqueous  $\text{TiO}_2$  suspension with light energy greater than band gap energy of the semiconductor (3.2-3.35eV), conduction band electrons and valence band holes are generated. Absorption of efficient photons ( $h\nu \geq E_G = 3.2 - 3.35 \text{ eV}$ ) by titanium.



$$E = h\nu = h \frac{c}{\lambda} \leftrightarrow 3.2 * 1.6 * 10^{-19} = 6.626 * 10^{-34} * 3 * \frac{10^8}{\lambda} \quad (4)$$

$$\lambda = 3.88 * 10^{-7} \text{ m} = 388 \text{ nm}$$

If band gap energy = 3.35 eV then  $\lambda = 370 \text{ nm}$

### 2.3. Temperature influence

Because of photonic activation, photocatalytic systems do not require heating and operate at room temperature. The true activation energy is nil, whereas the apparent activation energy is often very low (a few kJ/mol) in the medium temperature range (20°C-80°C). However, at very low

**Figure1:** Order regimes related to light intensity.

recombination rate,  $\theta$  is the fractional site coverage for the reactant. The decay rate is also affected by the organic molecules adsorbed on the surface of the catalyst.

### 2.2. Oxygen influence

In semiconductor photocatalysis for water purification, the pollutants are usually organics. Oxygen is very important for a complete mineralization of the pollutants and it does not seem to be competitive with other reactive during the adsorption on  $\text{TiO}_2$  because the places where oxidation takes place are different from those of reduction.

The Dissolved Oxygen adsorbs the free electrons on the catalyst surface, preventing the build-up of negative charged sites on the surface. If the electrons are not absorbed from the catalyst surface the chances of electron-hole recombination will increase dramatically and the reaction rate will decrease because of the limited number of positive charged sites where the hydroxyl radicals can be produced [25]-[27]. Therefore, injection of pure  $\text{O}_2$  becomes necessary in once-through experiments at low flow rates. At high flow rates or with recirculation, the addition of oxygen is not always necessary since the illumination time per pass is short. The water again recovers the oxygen consumed when it reaches the tank (open to the atmosphere and stirred) [28]-[29].

or pure oxygen ( $p = 1 \text{ atm}$ ) is not drastic. In an industrial plant it would be purely a matter of economy of design. temperatures (-40°C-0°C), activity decreases and activation energy becomes positive.

The decrease in temperature favors reactants adsorption, which is a spontaneous exothermic phenomenon, but also favors adsorption of the final reaction products, desorption of which tends to be the rate-limiting step. By contrast, at "high" temperatures (>70-80°C) for various types of photocatalytic reactions, the activity decreases and the apparent activation energy becomes negative.

When temperature increases above 80°C, nearing the boiling point of water, the exothermic adsorption of reactants is disfavored and this tends to become the rate-limiting step. In addition to these mechanical effects, other consequences of plant engineering must be considered. If temperature is high, the materials used for the plant should be temperature-resistant and oxygen concentration in water decreases.

Consequently, the optimum temperature is generally between 20 and 80°C. This absence of need for heating is attractive for

photocatalytic reactions carried out in aqueous media and in particular for environmental purposes (photocatalytic water purification). There is no need to waste energy heating water that already possesses a high thermal capacity [34].

#### 2.4. pH influence

The pH of the reactions have a significant impact on the adsorption of the substrate to the catalyst by affecting the surface charge and state of ionization of the compound. It also affects the nature of the metal oxide catalyst surface in terms of its surface charge [35].

The abundance of all the species as a function of pH:  $\text{TiOH} \geq 80\%$  when  $3 < \text{pH} < 10$ ;  $\text{TiO}^- \geq 20\%$  if  $\text{pH} > 10$ ;  $\text{TiOH}_2^+ \geq 20\%$  when  $\text{pH} < 3$ . Under these conditions, the photocatalytic At first sight a very acidic solution appears to be detrimental and a very basic solution to be favorable, since the variations are modest or non-existent around neutrality[30]. Other studies taking that Titanol (represented as  $>\text{TiOH}$ ) represents the primary hydrated surface functionality of  $\text{TiO}_2$ . It is a neutral surface species predominant over a broad range of pH.

Below pH 6, however, the  $\text{TiO}_2$  accumulates a net positive charge due to the increasing fraction of total surface sites present as  $>\text{TiOH}^+$ . At high pH,  $\text{TiO}_2$  is deprotonated and the surface has a net negative charge due to a significant fraction of total surface sites present as  $>\text{TiO}_2^-$  [31]-[32].

The rate of the photocatalytic process is therefore affected by the absorption of different solutes to the surface of the catalyst. At low pH, negatively charged ions such as  $\text{Cl}^-$  and  $\text{HCO}_3^-$  are attracted to the positively charged surface of  $\text{TiO}_2$  and may reduce the efficiency of the reaction. However, at high pH these anions have little or no effect because of the negatively charged surface. Consequently, repulsion of  $\text{OH}^-$  may also reduce the generation of hydroxyl radicals [33].

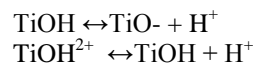
The rate of decomposition of the original substrate could yield an erroneous pH as the best for contaminant degradation. Therefore, a detailed analysis of the best pH conditions should include not only the initial substrate, but also the rest of the compounds produced during the process [36]-[37].

The ionization state of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions, respectively. The positive holes are considered the major oxidation species at low pH, whereas hydroxyl radicals are considered the predominant species at neutral or high pH [38]-[39]. The generation of  $\text{OH}^\bullet$  is expected to be higher due to the presence of more available hydroxyl ions on the catalyst surface. Thus, the degradation efficiency of the process is expected to be enhanced at high pH [31],[40].

#### 2.5. Pollutant Concentration

It is well known that in photocatalysis the degradation rate observed for an organic substrate follows the saturation behavior. After a certain concentration is achieved that the rate increments are very small and, in some cases, a decrease is observed.

The pH of the aqueous solution significantly affects  $\text{TiO}_2$ , including the charge of the particle and the size of the aggregates it forms. The PZC for  $\text{TiO}_2$  is around 7. Above and below this value, the catalyst is negatively or positively charged according to:



degradation of the ionisable organic compounds is affected by the pH.

The optimum contaminants concentration in water before the photocatalytic treatment must permit the maximum reaction rate. So, the initial concentration of contaminants in the wastewater can be optimized, when possible. Since hydroxyl radicals react not selectively, numerous intermediates are formed en-route to complete mineralization at different concentrations. Because of this, all tests have to be carried out using TOC as crucial parameter, because the photocatalytic treatment must destroy not only the initial contaminant, but all organic compounds.

As the reaction is not expected to follow simple models like first or zero order kinetics, overall reaction rate constants cannot be calculated. The complexity of the results, of course, is caused by the fact that the TOC is a sum parameter of ten including a lot of products that undergo manifold reactions.

It was reported in the literature, that the photocatalytic reaction occurs between the adsorbed substrate and  $\text{OH}^\bullet$  generated on  $\text{TiO}_2$  surface. The concentration of adsorbed substrate increases with increase in feed substrate concentration. However, for constant light intensity,  $\text{TiO}_2$  loading and dissolved oxygen concentration, the concentration of  $\text{OH}^\bullet$  remains practically same. However, adsorbed substrate concentration increases, the rate of photocatalytic degradation decreases due to a lower  $\text{OH}^\bullet$  [28]-[29].

Although different authors [28]-[29],[41]-[42] admit that the Langmuir-Hinshelwood (L-H) model is not a perfect explanation of the mechanism of the photocatalytic process, they do agree on its usefulness, since the behavior of the reaction rate versus reactant concentration can very often be adjusted to a mathematical expression with it.

#### 2.6. Relation among particle size, reactor diameter and $\text{TiO}_2$ concentration

Many researchers studied the influence of catalyst concentration on process efficiency [25];[34];[43]-[46].

The great difference existing between  $\text{TiO}_2$  from dry powder and  $\text{TiO}_2$  particles suspended in an aqueous medium is the mean size of the particles. If two samples having the same catalyst concentration but dispersed with different protocols (ultrasounds and stirring) are compared, sonicated samples

showed to be more efficient. Although in stirred samples there are fewer TiO<sub>2</sub> clusters, larger clusters screen light better than small one [28]-[29].

The photocatalytic experiments carried out by using different particle sizes of the same catalyst have demonstrated that the efficiencies was better when quantity, size particles (small is better) of catalyst, and reactor diameter are optimized to allow UV photons to penetrate along the entire photo reactor path length. In this case, it is not possible to talk about particle radius, because TiO<sub>2</sub> powder is irregularly shaped, and when it is dispersed in an aqueous medium the “particles” (300-600 nm sized) are clusters of primary particles (20-40 nm sized), not spherical or mono disperse [28]-[29];[25].

This leads to the conclusion that the light action, in colloidal suspensions, is a determining parameter for solar photo reactor. The increase in photodegradation with an increase in the catalyst concentration approaches a limiting value at high TiO<sub>2</sub> concentrations, and this limit depends on the total illumination of the TiO<sub>2</sub> particles; when the catalyst concentration is very high, turbidity hinders further penetration of light into the reactor [43]-[44].

The reaction rate constants increased linearly with TiO<sub>2</sub> concentration, which may be due to the increase in the total surface area of photocatalysts, namely number of active sites available for the photocatalytic reaction as the dosage of photocatalyst increased. A “screening” effect is produced when the TiO<sub>2</sub> concentration is very high.

Photocatalysis is a surface reaction; increasing the catalyst loading in a slurry the concentration of active sites increases in the fluid and, hence, the reaction rate within a range of concentrations. It is therefore necessary to find out the optimum catalyst concentration experimentally. Where the optimum value is known, as the minimum catalyst concentration, at which the maximum reaction rate reached.

A number of studies have shown that initially the reaction rate increases with the catalyst loading but after a certain limit; beyond the optimum level it decreases [21],[25],[40],[47].

The drop in the photocatalytic activity is due to an increased light scattering effect, particle agglomeration and poor light penetration in the solution generated by the high particle concentration. For this reasons, in a "slurry reactor", there is

On the same note, reducing flow rates in a thin film reactor can improve the contact time per pass, but at the same time it will drastically increase the chances of operating in mass transfer limited reactor with the consequent obvious inefficiency. Improving the photocatalytic surface in a specific volume will not give any positive effect to the final pollutant conversion if appropriate illumination is not guaranteed and yet illumination will be made more difficult due to the combined effect of the increased amount of catalyst and the extremely high light absorption coefficient characteristic of titanium dioxide.

design. It should also be recalled that small particle sizes caused additional problems for catalyst separation after photocatalytic treatment.

The best inner reactor diameter, for solar photocatalytic applications is in the range of a few centimeters with a few hundred mg of TiO<sub>2</sub> per liter. The area/volume ratio is also a crucial parameter, and if this ratio is optimized the reactor efficiency would also be increased [28]-[29].

Degussa P25TiO<sub>2</sub> is a highly photo reactive catalyst among many different kinds of TiO<sub>2</sub> (Anatase and rutile), which is generally known to have a slow electron-hole recombination rate. When TiO<sub>2</sub> concentration increases, more photons are absorbed by the catalyst, which in turn leads to higher concentrations of hydroxyl radicals and other reactive species which accelerate the degradation process.

the need of an optimum catalyst loading in order to reach the maximum level of photocatalytic activity [34];[43]-[44].

The percentage of photons absorbed by the suspension and the percentage of photons scattered by the TiO<sub>2</sub> particles is a very complex problem that cannot be solved experimentally, but must be experimentally estimated. The titanium dioxide employed in the photocatalytic experiments is disposed as a colloidal suspension [48]-[51].

## 2.7. Contact time and surface area

The contact time and surface area are some of the most important parameters for the success of a photocatalytic processes but are also some of the most difficult to increase. The controllable parameters that would improve the reaction rate also have detrimental effect on other aspects of the reaction making photocatalytic reactor engineering a big challenge.

Photocatalyst is a surface reaction; its efficiency is related to the chance that reactants have to interact with the catalyst when there is a positive charge available on its surface. There are different ways to improve the chances of contact between the pollutants and catalyst; for example it is possible to increase the catalyst surface in the reactor volume or decrease the flow rates to increase the residency time in the reactor [52].

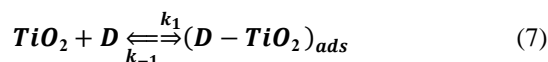
## 3. Mathematical Model Derivation

The mathematical model includes a set of variables that depend on each other to define a number of equations in terms of these variables.

When any physical equipment is being designed it is necessary to use mathematical modeling to save the time and effort, to optimize the operating conditions, to design control system, to maintain the process within safe operating limits and maximizing production and, finally, to avoid the expensive pilot plant experiments.

In this part of this research a mathematical model that described the drug removal by TiO<sub>2</sub> photocatalysis is proposed. Due to the complexity of the final equations of the model specific numerical solution is required and it is recommended to validate and solve this model numerically by a specialist in numerical techniques and solutions.

To derive the mathematical model of the drug removal by TiO<sub>2</sub> photo catalysis it is better to start from the initial concept of adsorbing the drug on the photo catalyst surface. This reaction is presented by equation (1):



where D - drug, (D - TiO<sub>2</sub>)<sub>ads</sub> - drug adsorbed on TiO<sub>2</sub>. At the end, the intermediary products can compete with the drug for adsorption sites on the catalyst's surface; refer to equation (12):

Based on the assumption that the adsorption obeys Langmuir conditions (one monolayer, catalyst surface energetically uniform, no interaction between adsorbed molecules and all the adsorption occurs by the same mechanism) from reactions presented in the equations 7 and 12 it is clearly that:

$$k_1 c (1 - \theta_D - \sum \theta_i) = k_{-1} \theta_D \quad (13)$$

$$k_i c_i (1 - \theta_D - \sum \theta_i) = k_{-i} \theta_i \quad (14)$$

Where Equations 13 and 14 lead to:

$$\theta_D = \frac{K_a c}{1 + \sum (K_i c_i) + K_a c} \quad (15)$$

Where  $K_a = \frac{k_1}{k_{-1}}$ ,  $K_i = \frac{k_i}{k_{-i}}$  and  $\theta_D$

is the fractional site coverage for the drug

The reactions presented by equations 10 and 11 give the variation of drug concentration (removal rate) as following:

$$\frac{dc}{dt} = -k_4 \theta_D [h^+] - k_5 \theta_D [HO \bullet] \tau \quad (16)$$

Where  $\tau$  – lifetime of the HO• radicals.

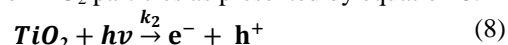
Hole-concentration varies in time and this variation can be expressed by taking into account reactions presented by equation 8, 9 and 10:

$$\frac{d[h^+]}{dt} = -k_3 [h^+] + k_{-3} [H^+] [HO \bullet] - k_4 [h^+] \theta_D + k_2 \sqrt{I} \quad (17)$$

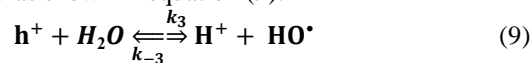
The last term of equation (17) represents hole rate generation (I - light intensity). Assuming stationary condition for HO•, While from equation (17) the hole rate is measured by:

$$-\frac{d[h^+]}{dt} = k_3 [h^+] \left( 1 + \frac{1}{1 + \frac{k_5 \theta_D}{k_{-3} [H^+]}} \right) + k_4 [h^+] \theta_D + k_2 \sqrt{I} \quad (21)$$

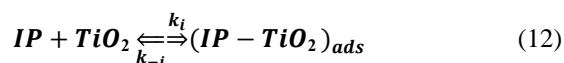
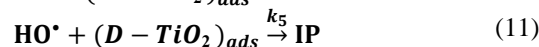
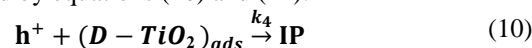
The photo catalysis process is based on hole-electron pair generation by light radiation, and this process takes a place on the surface of TiO<sub>2</sub> particles as presented by equation 8:



The generated holes will produce hydroxyl radicals reacting with H<sub>2</sub>O as shown in equation (9):



These radicals will convert the drug adsorbed on TiO<sub>2</sub> to intermediary products. Also the generated holes can react with the adsorbed drug leading to further intermediary products as expressed by equations (10) and (11):



i.e. formation rate = consumption rate the above equation converted to:

$$k_3 [h^+] = k_{-3} [HO \bullet] [H^+] + k_5 [HO \bullet] \theta_D \quad (18)$$

Where the hydroxyl radicals concentration can be obtained by equation (19):

$$[HO \bullet] = \frac{k_3 [h^+]}{k_{-3} [H^+] + k_5 \theta_D} \quad (19)$$

Substituting equation 19 into equation 16, the removal rate is obtained by equation (20):

$$-\frac{dc}{dt} = [h^+] \theta_D \left[ k_4 + \frac{k_3 k_5 \tau}{k_{-3} [H^+] + k_5 \theta_D} \right] \quad (20)$$

Equations 20 and 21 represent the main equations of the proposed mathematical model for drug removal by photocatalysis. This model accounts for removal rate depending on:

- Drug and intermediate products adsorption on TiO<sub>2</sub> surface ( $k_1, k_{-1}, k_i, k_{-i}$ )
- Light intensity, I.
- pH
- Temperature

## Conclusions

The photocatalytic treatment of a pharmaceuticals, from aqueous solution in a photocatalytic reactor was optimized. Effect of operational parameters on the removal efficiency of such pollutants were evaluated.

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- where r is the rate of mineralization, k is the reaction rate constant, C is the concentration, K is the adsorption coefficient and  $\theta$  is the fractional site coverage for the reactant as  $KC \ll 1$

The effect of these factors should be taking into account in order to establish the solution of the proposed model.

Factors affect the degradation rate :UV light intensity, oxygen concentration, temperature, pH, drug concentration, relation among particle size, reactor diameter and TiO<sub>2</sub> concentration, Contact time and surface area were investigated.

These factors were investigated and the kinetic parameters derived from the corresponding experimental data.

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