"HENRI COANDA"
AIR FORCE ACADEMY
ROMANIA

"GENERAL M.R. STEFANIK"
ARMED FORCES ACADEMY
SLOVAK REPUBLIC

INTERNATIONAL CONFERENCE of SCIENTIFIC PAPER
AFASES 2012
Brasov, 24-26 May 2012

PHOTOCATALYSIS PROCESSES USED FOR DISINFECTION. A MATHEMATICAL APPROACH

Violeta VASILACHE *, Elena AGHINIȚEI, Laura LELUȚIU***, Marius Dan BENȚA*****

*Stefan cel Mare University of Suceava, ** Industrial School Group Rasnov,
***Transilvania University of Brasov

Abstract: *In last decades, photocatalysis processes induced by titanium dioxide under UV and Visible electromagnetic radiation have shown a great potential in disinfection of water and air, also in degradation of many pollutants, especially organic pollutants. The procedure is a low-cost one, environmental friendly and sustainable. The energy consumption is almost zero or very low, because sometimes only solar radiation needed. Photocatalysis is an advanced oxidation technology which could remove persistent organic compounds and microorganisms from water and air. The mechanism of photocatalytic reactions need to be clarified, in particular inactivation of bacteria.This paper reviews some mathematical models of disinfection, which correlates experimental data with theoretical suppositions and hypothesis. The biochemical processes are very complex and a lot of parameters need to be taken into account. A mathematical model has to be as simple as it is possible. The aim is to utilize a multi-variables optimization approach to find the optimum parameters needed to control and enhance the photo-disinfection efficiency process.*

Keywords: *photocatalysis, kinetics, bacteria inactivation, mathematic models*

1. INTRODUCTION

Degradation and pollution of the environment forced research in the field of protection and restoration. Advanced oxidative processes offer good perspectives in degradation of pollutants and disinfection. Photocatalysis is an advanced oxidative process which consists in production of high reactive species under the action of UV or Visible radiation on a photo catalyst surface. Titanium dioxide is the most important photo catalyst due to specific properties as width of the band gap, low cost and abundance. Figure 1 presents a scheme of the photocatalytic process [1, 2].

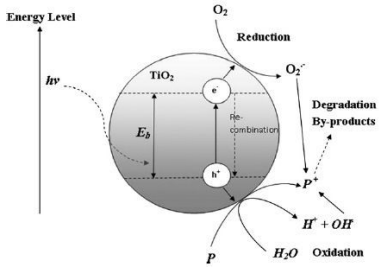

Figure 1. Photocatalysis: electron-hole pairs on titanium dioxide surface and reactive species forming

The stages of photocatalytic reactions are presented as follows:

a. Generation of mobile charge particles under the action of a radiation with hν>3.16 eV (E_g value for TiO_2 anatas): electrons (e^-) in conduction band and holes (h^+) in valence band:

$$2TiO_2 + h\upsilon \Leftrightarrow TiO_2(e^-) + TiO_2(h^+) \quad (1)$$

b. Recombination of electron-hole pairs:

$$TiO_2(e^-) + TiO_2(h^+) \Leftrightarrow 2TiO_2 + heat, light \quad (2)$$

c. Reactions on photo catalyst surface:

The holes are strong reducers and directly oxidize compounds, or react with electron donors like water or hydroxyl ions, forming hydroxyl radicals (reaction 3). Hydroxyl radicals form on TiO_2 surface by reaction through holes from valence band and water molecules or adsorbed hydroxyl ions (reactions 4-5).

$$TiO_2(h^+) + \mathrm{Re}\,d_1 \Leftrightarrow Ox_1^+ + TiO_2 \quad (3)$$

$$TiO_2(h^+) + H_2O \Leftrightarrow OH* + H^+ + TiO_2 \quad (4)$$

$$TiO_2(h^+) + HO^- \Leftrightarrow OH* + TiO_2 \quad (5)$$

Photogene rated electrons react with oxygen forming superoxide radicals (O_2^-*) (reaction 6). Superoxide radicals react with protons forming free radicals HO_2* (reaction 7) which further forms O_2 molecules and H_2O_2 (reaction 8). Electrons from conduction band react with oxidative species (reaction 9).

$$TiO_2(e^-) + O_2 \Leftrightarrow O_2^{-*} + TiO_2 \quad (6)$$

$$O_2^{-*} + H^+ \Leftrightarrow HO_2^* \quad (7)$$

$$2HO_2^* \Leftrightarrow O_2 + H_2O_2 \quad (8)$$

$$TiO_2(e^-) + Ox_2 \Leftrightarrow \mathrm{Re}\,d_2^- + TiO_2 \quad (9)$$

d. Degradation:

Radicals and ions formed on photo catalyst surface could:

► react with adsorbed compounds on photo catalyst surface;

► diffuse from photo catalyst surface into solution to participate further on chemical reactions;

► recombine by electrons transfer reactions – this process has to be limited because it is responsible by low efficiency of photodegradation process.

2. KINETICS AND MODELING

Kinetics and mecanism of photocatalytic reactions in photomineralization or photo-disinfection rate of the water contaminants are useful to study the whole process. Different kinetics and rate model for both photomineralization and photo-disinfection are discussed in this section [3-5].

2.1. Kinetisc of photocatalytic reactions: photomineralization and photo-desinfection

Kinetic or mechanism studies about irradiated TiO_2 surfaces usually focussed only on a single constituent model organic compound. It was found that Langmuir-Hinshelwood (L-H) kinetic describes satisfactory photocatalyitc reactions. According this model the photocatalytic reaction rate (r) is proportional to the fraction of surface coverage by the organic substrate (Q_x), k_r is the reaction rate constant, C is the concentration of organic species and K is the Langmuir adsorption constant:

$$r = -\frac{dC}{dt} = k_r\theta_x = \frac{k_r KC}{1+KC} \quad (10)$$

Eq. (10) could be solved considering initial concentration C_0 in a reference point, as follow:

$$\ln\left(\frac{C}{C_0}\right)+K(C-C_0)=-k_rKt \quad (11)$$

The value for K could be obtained by linearization of Eq. (10), where 1/r is rated at 1/C:

$$\frac{1}{r_0}=\frac{1}{k_r}+\frac{1}{k_rKC_0} \quad (12)$$

When the concentration of organic compounds is low, and noted k' = k_rK,

$$r=-\frac{dC}{dt}=k_rKC=k'C \quad (13)$$

$$C=C_0e^{-k't} \quad (14)$$

$$\ln\left(\frac{C_0}{C}\right)=-k_rKt=-k't \quad (15)$$

This could be represented as in fig.2 (rate constant k vs. catalyst loading), and it is satisfactory for designing great majority of photochemical reactors.

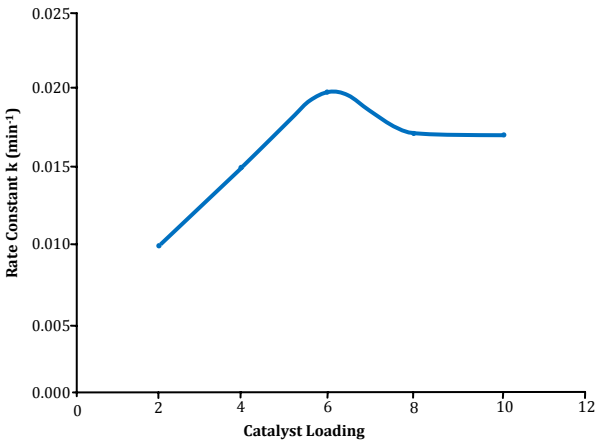

Figure 2. Usually representation of saturation kinetic for degradation of an organic compound in a photocatalytic reactor

2.2. Kinetics of photo-disinfection reactions

Eq. (16) describes a photo-disinfection reaction, assuming that the concentration of the photo catalyst is constant during irradiation.

$$\frac{dN}{dt}=-kmN^xC^nT^{m-1} \quad (16)$$

where dN/dt is inactivation rate, N is number of surviving bacteria after irradiation time t, k is experimental constant rate, C is concentration of used photo catalyst and m, n, x empiric constants. Chick-Watson (C-W) model is the most used for studies about photo-disinfection in a simple hypothesis regarding the mechanism and it is described by Eq. (17).

$$\frac{\log N}{N_0}=-k'T \quad (17)$$

C-W model describes photo-disinfection rate like a linear function of bacteria number and photo catalyst charge. Fig. 3 shows a representation of C-W model, fig. 4 the modified C-W equation (Eq. (18)).

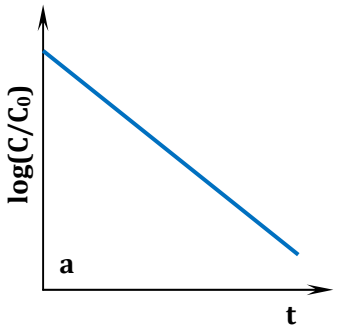

Figure 3. Chick-Watson model representation

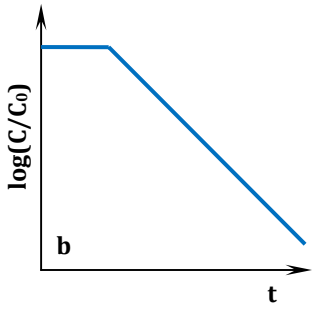

Figure 4. Modified C-W model representation

$$\frac{\log N}{N_0} = -k' C^n T^m \qquad (18)$$

Eq. (19) characterizes Hom model, represented in fig. 5 while fig. 6 presents the modified Hom model (Eq. (19)).

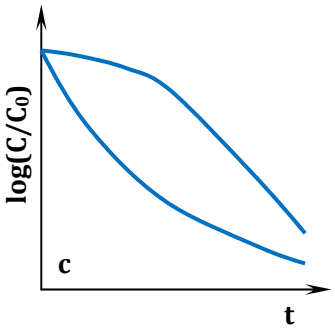

Figure 5. Hom model representation

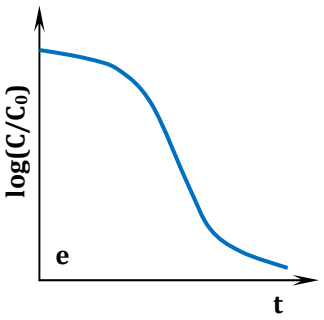

Figure 6. Modified Hom model representation

$$\frac{\log N}{N_0} = -k_1 \left[1 - \exp\left(-k_2 t\right)\right]^{k_s} \qquad (19)$$

Marugan et al. (2008) found in their studies those three regions (a shoulder, a linear one and the tail) specific in many photo-disinfection processes [6]. They used a commercial form of the titanium dioxide, named Degussa P-25. The first region is an initial delay, called "shoulder" which could be explain like a resistance of the bacteria before chemical reactions will perforate their cellular membrane. For the second region, a linear behavior was observed in the great majority of studies. The third region or the "tail" is not understood completely. Some researchers justified it like a competition through different secondary compounds which appear during photochemical reactions and other reactions caused by degradation of inactivated bacteria cells. Other researchers explained the "tail" as

a resistance of a number of bacteria from whole population.

Even the processes have to be clarified in the terms of accuracy, the empiric experimental and theoretical data could offer information for designing photocatalytic systems for disinfection.

3. CONCLUSIONS & ACKNOWLEDGMENT

Photocatalysis offers good perspectives regarding depollution and disinfection of air and water.It is an environmental friendly procees. The mechanism and the kinetics of reactions have to be clarified. Mathematical models provide information for designing practical disinfection systems.

This paper was supported by the project "Progress and development through post-doctoral research and innovation in engineering and applied sciences– PRiDE - Contract no. POSDRU/89/1.5/S/57083", project co-funded from European Social Fund through Sectorial Operational Program Human Resources 2007-2013.

REFERENCES

1. LANCASTER M., Green chemistry: An introductory text, Royal Society of Chemistry, London, (2010).

2. HUNGER M., HUSKEN G., BROUWERS H.J.H., Photocatalytic degradation of air pollutants — From modeling to large scale application, *Cement and Concrete Research* 40. 313–320 (2010).

3. SANCHEZ F., SOBOLEV K., Nanotechnology in concrete – A review, *Construction and Building Materials* 24. 2060–2071 (2010).

4. LAMBERT R.J.W., JOHNSON M.D., The effect of interfering substances on the disinfection process: a mathematical model, *Journal of Applied Microbiology* 91. 548-555 (2000).

5. CHOMG M.N., JIN B., CHOW C.W.K., SAINT C., Recent developments in photocatalytic water treatment technology: A review, *Water Reseearch* 44. 2997-3027 (2010).

6. MARUGAN J., van GRIEKEN R., SORDO C., CRUZ C., Kinetics of the photocatalytic disinfection of Escherichia coli suspensions, *Applied Catalysis B: Environmental* 82. 27-3 (2008)