A COMPARISON BETWEEN BULK AND SUPPORTED TiO$_2$ PHOTOCATALYSTS IN THE DEGRADATION OF FORMIC ACID

A. R. Tôrres[1], E. B. Azevedo[1], N. S. Resende[2] and M. Dezotti[2*]

[1]Chemistry and Environment Department, Faculdade de Tecnologia,
Universidade do Estado do Rio de Janeiro, Telefax: +(55) (24) 3354-0194/7875,
Estrada Resende-Riachuelo, s/nº, Morada da Colina, 27523-000, Resende - RJ, Brazil
E-mail: artorres@fat.uerj.br, E-mail: bessa@fat.uerj.br
[2]NUCAT, Programa de Engenharia Química, COPPE, Universidade Federal do Rio de Janeiro,
Centro de Tecnologia, Bloco G, Sala 117, Phone: +(55) (21) 2562-8348,
Fax: +(55) (21) 2562-8300, PO Box: 68502, 21945-970, Rio de Janeiro - RJ, Brazil
E-mail: neuman@peq.coppe.ufrj.br
[2]Water Pollution Control Lab, Programa de Engenharia Química, COPPE,
Universidade Federal do Rio de Janeiro, Centro de Tecnologia, bloco G, sala 115,
Phone: +(55) (21) 2562-8347, Fax: +(55) (21) 2562-8300,
PO Box: 68502, 21945-970, Rio de Janeiro - RJ, Brazil
E-mail: mdezotti@peq.coppe.ufrj.br

Abstract - The photocatalytic activity of bulk and supported TiO$_2$ catalysts were tested using formic acid as a probe molecule. The supported catalysts tested were prepared by impregnation using aluminum oxide (Al$_2$O$_3$) as the support and the bulk catalysts by precipitation, both in sol-gel systems. For purposes of comparison, a photocatalyst supplied by DEGUSSA (P25) was also tested. The photolysis rate was found to be less significant than the photocatalytic rate. The Langmuir-Hinshelwood model was adopted and its constants were estimated and used to compare the various catalysts. The supported catalysts showed no significant activity, in spite of their high specific surface area. The bulk catalysts tested showed the highest photocatalytic rates. The adsorption constants determined experimentally were different from the ones estimated based on the kinetic experiments. The parameter estimation procedures tested were used to clarify this issue.
Keywords: Photocatalysis; Catalyst; Formic acid; TiO$_2$

INTRODUCTION

According to Herrmann (1999) and Plaza and Malato (1999), the use of bulk TiO$_2$ photocatalysts, mainly in the anatase crystalline phase, in the degradation of recalcitrant substances in wastewaters is a widespread technique. It has also been used in the elimination of toxic compounds from atmospheric emissions (Nicolella and Rovatti, 1998). TiO$_2$ is used due to its semiconductor properties and to the generation of electron-hole pairs under UV irradiation (Hoffmann et al., 1995). TiO$_2$ photocatalysts have been prepared by several routes and methods, as depicted by Watson et al. (2003), Cólon et al. (2002), and Saadoun et al. (2000). The photocatalysts usually used have a specific surface area of approximately 50 m^2 g^{-1}, e.g. the P25 manufactured by Degussa, whose composition is 70% anatase and 30% rutile (Ettinger, 1995). Several authors report different behaviors for anatase and for other crystalline forms of titanium dioxide (rutile and brookite), with the first being better for

*To whom correspondence should be addressed

photocatalytic purposes. The preparation of supported photocatalysts, in which anatase is also the predominant form has also been reported. The main advantage of supported catalysts is the large specific surface area, due to the support, as suggested by Loddo et al. (1999).

It is believed that the generation of the electron-hole pair occurs only on the solid surface, although its diffusion and recombination occur in the solid volume, as described by Serpone and Pelizzetti (1989). Therefore, the existence of a compatible crystalline structure underneath the surface layer indicates that solids with a bulk active phase should have increased photocatalytic activity.

Through regression procedures, kinetic and adsorption constants are obtained. These procedures are sometimes simplified to obtain linear relationships (in fact, a model that corresponds to the straight line equation). The most complete approach to parameter estimation is to consider the experimental errors of all variables in the model.

MATERIALS AND METHODS

Solids and Photocatalysts

The solids used in the photocatalytic tests were prepared at PEQ/COPPE/UFRJ using the impregnation technique, as described in Table 1. For comparison purposes, experiments were performed with the P25 photocatalyst produced by Degussa (whose characteristics are also presented in Table 1). The solids were obtained by precipitation by the sol-gel technique, using titanium isopropoxide (Hague and Mayo, 1994) in accord with the procedure proposed by Egues (2002). For the final conversion to oxide, the precipitates were annealed at 823 K. The solid named *PC100* is composed of pure TiO_2 (bulk catalyst). The solids named *PC13* and *PC5* were obtained by impregnation of TiO_2 on alumina (supported catalysts).

Table 1: Solids used in the tests.

| Solids	% w/w TiO_2	% Anatase*	S $(m^2\,g^{-1})$	Annealing Temperature (K)
PC100	100	100	60	823
PC13	13	100	190	823
PC5	5	100	180	823
P25	100	70	50	—
Al_2O_3	—	—	197	—

*On the catalyst surface.

Test Molecule: Formic Acid

Throughout the experiments, formic acid was used as the test molecule. This probe molecule was chosen because no intermediates are generated during its oxidative decomposition (Equation 1).

$$HCOOH + \tfrac{1}{2} O_2 \rightarrow CO_2 + H_2O \qquad (1)$$
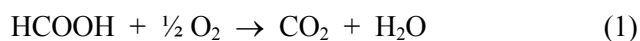
The use of this molecule is suggested by Davydov and Smirniotis (2000) and Ito et al. (1999). The formation of bicarbonate ion may be considered, although the air flow supplying oxygen to the solution is capable of stripping the carbon dioxide generated, keeping the bicarbonate concentration insignificant due to the shift in equilibrium (Equation 2). The remaining formic acid was determined by acid-base titration (Bideau et al., 1980). Careful choice of the base (sodium hydroxide) concentration, elimination of the residual CO_2, and the use an adequate indicator, allow this method to be used without any problems.

$$CO_2 + 2\,H_2O \rightarrow HCO_3^- + H_3O^+ \qquad (2)$$
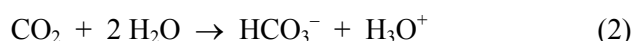
Adsorption Experiments

Using the P25 from Degussa, dark adsorption experiments were performed. The catalyst was kept in contact with solutions of formic acid for 24 hours with occasional stirring in order to achieve equilibrium. Four different solids masses were used to draw the isotherm. The equation used to calculate the adsorption constant is given as

$$q = q_m \frac{K_A C_{eq}}{1 + K_A C_{eq}} \qquad (3)$$

Photocatalytic and Photolytic Experiments

a) Photocatalysis

Reactions were conducted in a batch reactor with the catalyst suspended by magnetic stirring. A 250

W, medium pressure, Hg-vapor lamp was used for irradiation. It was kept 12 cm from the suspension surface, supplying a radiant flux of 108 J m^{-2} s^{-1} for wavelengths longer than 254 nm. Throughout the experiments, air was bubbled into the suspension by a diaphragm pump. This apparatus is reported by Azevedo (2003) and Azevedo et al. (2004).

The solids *PC100*, *PC13*, and *PC5*, along with the P25 photocatalyst (for comparison purposes) were tested. The suspension concentration was 500 mg L^{-1}. The irradiated volume was 100 mL for the solids (50 mg in suspension) and 200 mL for the P25 (100 mg in suspension).

b) Photolysis

These experiments were conducted as described previously, but without catalyst and air. This kind of experiment is aimed at isolating the UV decomposition, as formic acid absorbs light in the range of 206 to 212 nm.

c) Kinetic Model

The Langmuir-Hinshelwood approach was used (Equation 4). The catalyst mass (m_{cat}) in suspension was explicitly used in the model as, according to Herrmann (1999), the kinetic rate increases with it.

$$r = \frac{dC}{dt} = m_{CAT} \frac{k_{AB}K_A C}{1+K_A C} \qquad (4)$$

For the photolytic experiments, two kinetic models (zero- and first-order) were adopted, as described by Equations 5 and 6, respectively.

$$r = \frac{dC}{dt} = k_{AB}^{photolysis} \qquad (5)$$

$$r = \frac{dC}{dt} = k_{AB}^{photolysis} C \qquad (6)$$

RESULTS AND DISCUSSION

Adsorption Experiments

The experiments were initially performed with the TiO$_2$ Degussa P25. The experimental data are presented in the isotherm in Figure 1. The estimated parameters are shown in Table 2. A difference in parameters, depending on the estimation method used can be observed. For the original model, the maximum likelihood method was used and the errors of all variables involved were taken into account; for the linearized model, the least squares method was used. The variables were the equilibrium formic acid concentration (C_{eq}) and the mass ratio of adsorbate and adsorbent (q). The estimation procedure was performed using the ESTIMA and MAXIMA codes (Noronha et al., 1993).

By analyzing the results in Table 2, it can be observed that the two sets of parameters are quite similar, and in terms of the experimental errors presented in Figure 1, both sets represent the experimental data equally well. With the correlation matrix generated by the ESTIMA code (Figure 2), a strong correlation between the parameters can be seen. This fact was expected due to the structure of the model adopted. Therefore, the confidence range is stretched (Figure 1).
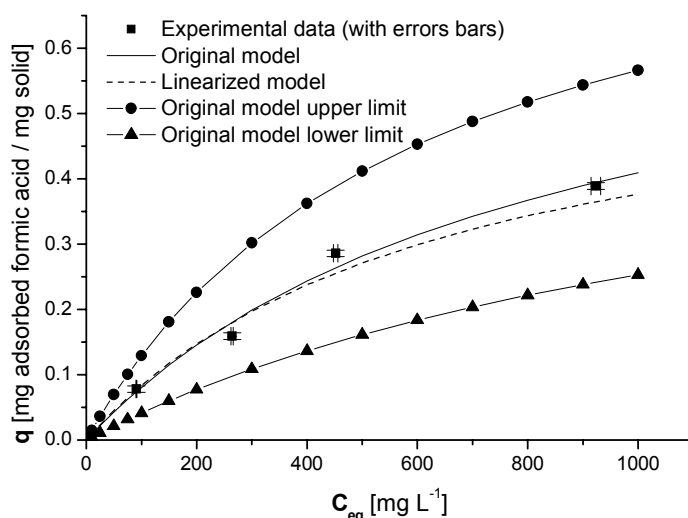
Figure 1: Isotherm for formic acid adsorption on TiO$_2$ (P25 Degussa).

Table 2: Formic acid adsorption on TiO$_2$ (P25 Degussa)

Model	q_m	K_A	CC*
original	0.748	1.21×10^{-3}	0.991
linearized	0.618	1.56×10^{-3}	0.991

*Correlation coefficient of experimental data and model results.

$$\begin{bmatrix} 1.00000 & -0.89246 \\ -0.89246 & 1.00000 \end{bmatrix}$$

Figure 2: Model parameters correlation matrix.

In all adsorption calculations, the following errors were considered: ± 0.5 mg L^{-1} for concentrations and $\pm 1.0 \times 10^{-3}$ for the ratio q. It is possible to estimate the errors of the parameters with the maximum likelihood estimation procedure. Therefore, the constants were:

- $q_m = 0.748 \pm 0.160$ and
- $K_A = 1.21 \times 10^{-3} \pm 0.450 \times 10^{-3}$ L mg^{-1}.

In order to check the difference between the real adsorption constant and the apparent one, three experiments were performed to obtain the adsorption constant of the *PC100* solid. The same procedure as

that adopted previously was used. The results obtained are presented in Table 3.

For this catalyst, the constant figures were

- $q_m = 0.189 \pm 0.259$ and
- $K_A = 0.356 \times 10^{-3} \pm 0.636 \times 10^{-3}$ L mg^{-1}.

It can be seen that the error magnitudes are greater than the constants themselves. Therefore, the significance of these parameters is questionable, even though a good correlation coefficient was observed (0.989). This kind of information cannot be obtained by estimation procedures like the least squares one.

Table 3: Formic acid adsorption on *PC100*

Model	q_m	K_A	CC*
original	0.189	0.356×10^{-3}	0.989
linearized	0.0558	2.61×10^{-3}	0.936

*Correlation coefficient of experimental data and model results.

Photolysis

The results obtained for the zero- and first-order kinetic expressions are presented in Table 4. The parameter estimation procedures were also compared, with the original model always used with the maximum likelihood method and the linearized model with the least squares one. It is noteworthy that, as a differential equation was used, an integration method was used simultaneously with the parameter estimation procedure. The integration routine used was the DASSL (Petzold, 1989).

By analyzing the results in Table 4, it can be seen that the original model with first-order kinetics is more suited to describing the experimental data. In Figure 3, it becomes clear that photolysis is not significant in the formic acid mineralization, as after 90 minutes only 15% had been removed.

In all photolysis calculations, the following errors were considered: ± 0.5 mg L^{-1} for concentrations and ± 0.25 minutes for time. Therefore, the constant figure was

- $k_{AB}^{photolysis} = 2.49 \times 10^{-3} \pm 0.433 \times 10^{-3}$ mg L^{-1} min^{-1}.

Table 4: Formic acid photolysis

Model	Order	k_{AB}	C_0	CC*
original	0	0.739	328	0.922
	1	2.49×10^{-3}	328	0.928
linearized	0	0.514	314	0.886
	1	1.73×10^{-3}	314	0.898

*Correlation coefficient of experimental data and model results.
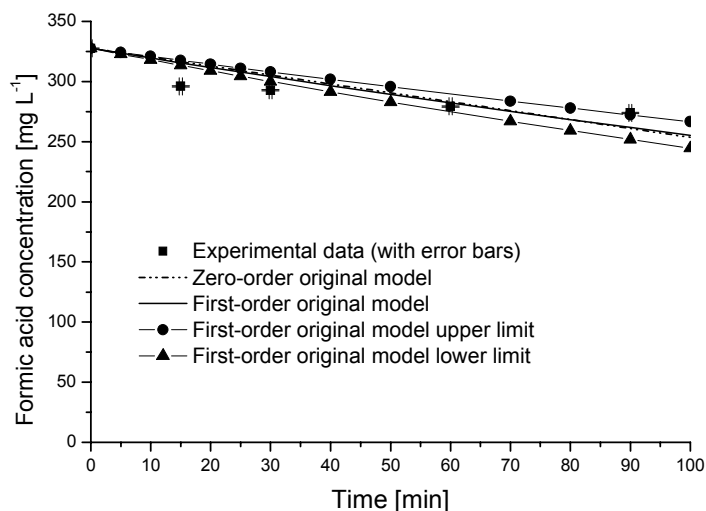
Figure 3: Formic acid photolysis.

Photocatalysis

a) P25 Photocatalyst

Five experiments were performed in order to obtain its characteristic parameters for the formic acid and the experimental setup in particular. The initial concentration of the formic acid was 310 ± 0.5 mg L^{-1}. The results achieved are presented in Table 5 and Figure 4.

Another significant result is the correlation coefficient between the parameters k_{AB} and K_A, which was - 0.979, indicating that they are strongly correlated. The introduction of the CO_2 competitive adsorption constant during parameter estimation, as suggested by Azevedo (2003) and Azevedo et al. (2004), was not successful because it resulted in a nonsignificant parameter.

b) *PC100* Solid

Three experiments were performed in order to estimate the Langmuir-Hinshelwood parameters. The initial concentration of the formic acid was 287 ± 0.5 mg L^{-1}. The results achieved are presented in Table 6 and Figure 5.

Table 5: Photocatalysis with P25.

Method	k_{AB}	K_A	CC*
Maximum likelihood	4.41×10^{-2}	2.25×10^{-2}	1.00
Maximum likelihood**	2.13×10^{-1}	1.21×10^{-3}	0.998
Least squares	5.13×10^{-2}	1.27×10^{-2}	0.995

*Correlation coefficient of experimental data and model results.
** Only k_{AB} was estimated; K_A was taken from adsorption experiments.
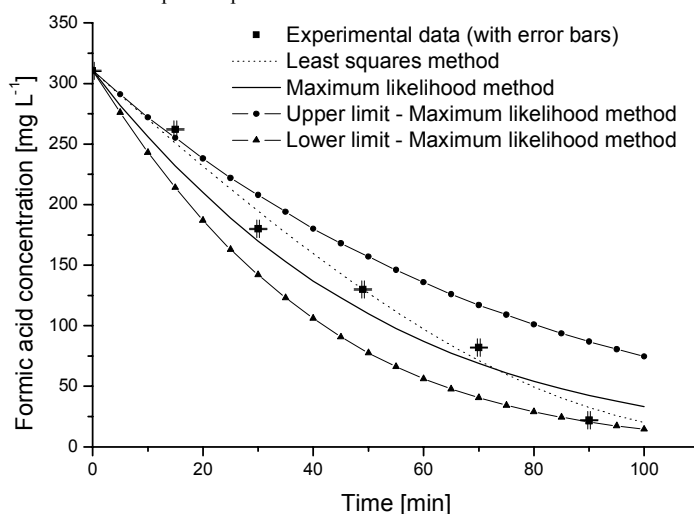
Figure 4: Formic acid photocatalysis with P25 Degussa.

Table 6: Photocatalysis with *PC100*.

Method	k_{AB}	K_A	CC*
Maximum likelihood	3.92×10^{-1}	4.05×10^{-3}	1.00
Maximum likelihood**	3.10×10^{0}	3.56×10^{-4}	1.00
Least squares	2.44×10^{-1}	1.04×10^{-2}	0.996

*Correlation coefficient of experimental data and model results.

** Only k_{AB} was estimated; K_A was taken from adsorption experiments.
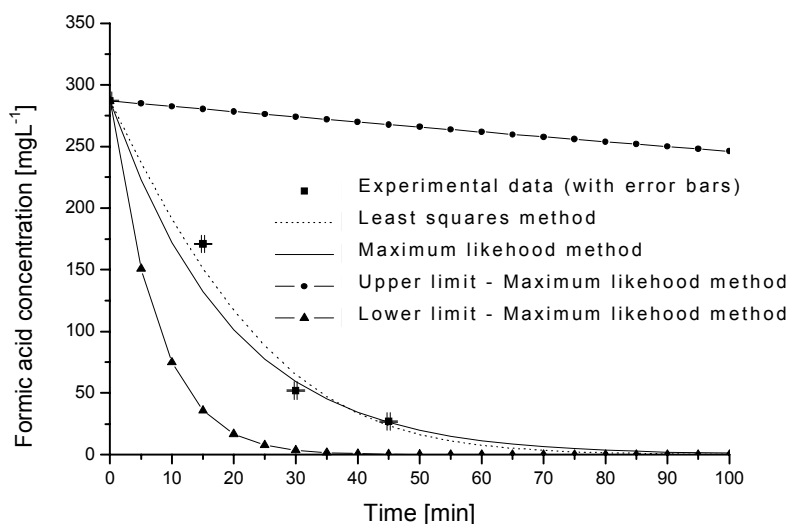
Figure 5: Formic acid photocatalysis with *PC100*.

c) Supported Catalysts (*PC13* and *PC5*)

The *PC13* solid showed no photocatalytic activity at all, even after 30 minutes of irradiation. The *PC5* solid had very little photocatalytic activity, as depicted in Figure 6, where its activity is compared to those of the P25 and *PC100*. These results are compatible with those obtained by Loddo et al. (1999), suggesting that it is necessary for the anatase layer to be thick enough so that a complete and characteristic crystalline phase is formed. This is a *sine qua non* condition for adequate adsorption and maintenance of the necessary charge carrier separation (avoiding their recombination), resulting in photocatalytic activity.
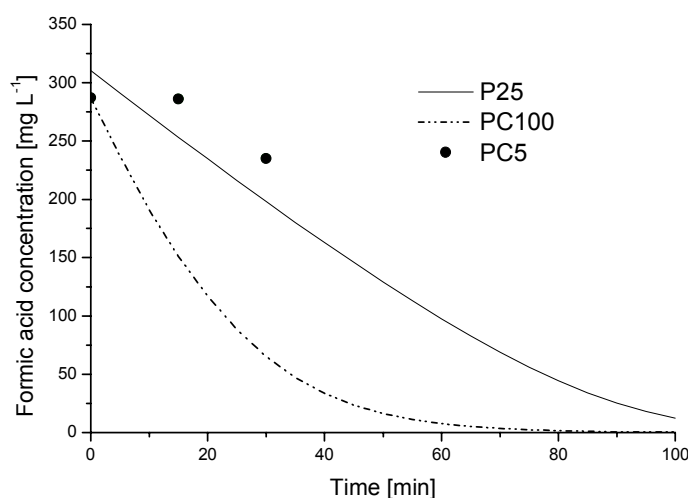
Figure 6: Comparison between *PC100, PC5*, and P25 Degussa.

CONCLUSIONS

The results obtained confirm the hypotheses regarding bulk photocatalysts characteristics, making clear the lack of photocatalytic activity of the supported catalysts. *PC13* and *PC5* supported catalysts showed insignificant reaction rates, while *PC100* had an initial reaction rate 2.43 times that of the P25.

The adsorption constants estimated for the photocatalysts P25 and *PC100* in independent experiments were different from the ones estimated in the kinetic experiments. This fact reinforces the concept of *apparent adsorption constant*, that is, a constant different from the real one due to reaction and mass transport aspects.

The adsorption and kinetic constants were obtained through simultaneous solution of the set of differential equations of the kinetic model. The adsorption constant, although strongly correlated with other parameters, gave coherent results when the maximum likelihood estimation procedure was used.

The results allow one to conclude that bulk catalysts have enhanced photocatalytic activity, making it necessary to develop preparation methods that produce solids with larger specific surface areas and higher concentrations of surface anatase.

As the adsorption and kinetic constants are used for comparing catalysts, their estimation errors and significance must be analyzed. P25 and *PC100* catalysts had quite different photocatalytic behaviors. This can be observed regardless of the model, the estimation procedure, and the type of adsorption constant. However, when the parameter confidence intervals are assessed for a variation of $\pm$ 1σ (standard deviation), the differences between the catalysts are not statistically significant. There is a significant superimposition of the confidence regions. Moreover, the establishment of a $\pm$ 1σ deviation means a confidence interval of less than 90%. Even at this confidence level, the validity of some parameters, such as the adsorption parameters for *PC100*, should be discussed.

These comparisons were mainly made in order to draw attention to the use of estimation procedures without the experimental errors associated with the parameters or that do not evaluate these errors. The results presented are valid for guiding in the preparation of photocatalysts, although there is still the need to perform additional experiments to further clarify this issue.

NOMENCLATURE

C	formic acid concentration,	mg L^{-1}
C_{eq}	formic acid equilibrium concentration,	mg L^{-1}
CC	correlation coefficient between the estimated figures and the experimental data	(-)
$k_{AB}^{photolysis}$	photolytic kinetic constant,	mg L^{-1} min^{-1} (zero-order) and min^{-1} (first-order)
k_{AB}	photocatalytic kinetic constant,	mg L^{-1} mg$_{TiO_2}^{-1}$ min^{-1}
K_A	formic acid adsorption equilibrium constant,	L mg^{-1}
m_{cat}	mass of catalyst in suspension,	mg
q	equilibrium mass ratio of adsorbate to adsorbent	(-)
q_m	initial mass ratio of adsorbate to adsorbent	(-)
r	kinetic rate of reaction,	mg L^{-1} min^{-1}
t	elapsed time,	min

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