

Experimental and mathematical evaluation of molecular adsorption models for organic pollutants on TiO₂-P25 particles

Evaluación experimental y matemática de modelos de adsorción molecular para contaminantes orgánicos en partículas de TiO₂-P25

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Abstract

In this work we evaluated conventional models based on adsorption isotherms of L2 type for organic compounds: DCA, phenol and 4-chlorophenol over TiO₂-P25 particles to different operational conditions. The models studied were Langmuir-Hinshelwood, Redlich-Petersen and Toth because these models can be applied as possible equations to improve the description of the reaction rate mechanism based on hydroxyl radical attack, and the degradation using heterogeneous photocatalysis. Finally the models were compared with experimental data for determination of the more appropriate isotherm. L-H model was the more appropriate and the results were high effective in the prediction of experimental data.

Keywords: *TiO₂-P25 photocatalyst, Organic compounds: DCA 4-Chlorophenol and Phenol, L2 isotherm.*

Resumen

Se evaluaron modelos convencionales de adsorción molecular basados en isoterma del tipo L2 para compuestos orgánicos ácido dicloroacético, fenol y 4-clorofenol sobre partículas de TiO₂-25 a diferentes condiciones de operación. Los modelos estudiados fueron Langmuir-Hinshelwood, Redlich-Petersen y Toth puesto que estos modelos pueden ser aplicados como posibles ecuaciones para mejorar la descripción de los mecanismos de velocidad de reacción basados en ataque de radicales hidroxilo y degradación usando fotocatalisis heterogénea. Los modelos fueron comparados con datos experimentales para determinar la isoterma más adecuada. El modelo L-H fue el mas apropiado y los resultados fueron de alta efectividad en la predicción de los datos experimentales.

Palabras Clave: *Fotocatalizador TiO₂-P25, Compuestos orgánicos: DCA, fenol y 4-clorofenol, Isoterma L2.*

1. Introduction

The rapid development of industrialization has carried the increase of pollution of one of more important natural resources, the water. Many pollutants discharged inside hydric sources cannot be biological treatment by conventional methods. In the present, the Advanced Oxidation Technologies (AOT's) are an alternative for wastewater treatment due to the mineralization capacity of recalcitrant compounds (Chong, *et al.*, 2012). The photocatalysis is contained in AOT's, which occur by electron-holes generation on the semiconductor surface for effect of radiation energy absorption with specific wavelength (Chong, *et al.*, 2010).

The photocatalysis has five fundamental steps: *i*) molecular adsorption of: water, hydroxyl ions, oxygen and reactive compounds (molecules of

substrate) [Ri], *ii*) radiation energy absorption for semiconductor and electron-holes generation (activation), *iii*) Recombination, *iv*) capture of photogenerated species (electron-holes), *v*) hydroxyl radical attack (see Table 1) (Turchi & Ollis, 1990).

In this mechanism the main way of the reaction is the oxidation for cracking of carbon-hydrogen bonds by hydroxyl radicals attack, which are generated for charge transfer to the holes h^+ from semiconductor adsorbed species (hydroxyl ions or water molecules).

The hydroxyl radicals can interact in different ways: with the solid surface by irreversible reactions; generation of transition reactions with adsorbed molecules; or migrate to the interface inside Helmholtz layer and finally react with

Table 1. Heterogeneous photocatalysis mechanism based on hydroxyl radical attack. Adapted from Turchi & Ollis, 1994.

Step	Reaction	
Adsorption	$O_L^{2-} + Ti^{IV} + H_2 \leftrightarrow O_L H^- + Ti^{IV} \int OH^-$	M1a
	$Ti^{IV} + H_2O \leftrightarrow Ti^{IV} \int H_2O$	M1b
	$Site + R_i \leftrightarrow R_{i,ads}$	M2
Activation	$TiO_2 + hv \rightarrow e_{BC}^- + h_{BC}^+$	M3
	$OH + Ti^{IV} \leftrightarrow Ti^{IV} \int OH$	M4
Recombination	$e^- + h^+ \rightarrow heat$	M5
Electron-Holes capture	$Ti^{IV} \int OH^- + h^+ \leftrightarrow Ti^{IV} \int OH$	M6a
	$Ti^{IV} \int H_2O + h^+ \leftrightarrow Ti^{IV} \int OH + H^+$	M6b
	$R_{i,ads} + h^+ \leftrightarrow R_{i,ads}^+$	M7
	$Ti^{IV} + e^- \leftrightarrow Ti^{III}$	M8a
	$Ti^{III} + O_2 \leftrightarrow Ti^{IV} \int O_2^-$	M8b
Hydroxyl radical attack	$Ti^{IV} \int OH + R_{i,ads} \rightarrow Ti^{IV} + R_{j,ads}$	M9a
	$OH + R_{i,ads} \rightarrow Ti^{IV} + R_{j,ads}$	M9b
	$Ti^{IV} \int OH + R_i \rightarrow Ti^{IV} + R_j$	M10a
	$OH + R_i \rightarrow Ti^{IV} + R_j$	M10b

free compounds. The trapped holes by organic molecules are considered with low reactivity; therefore, the main attack is by effect to hydroxyl radicals in the Helmholtz layer. Meanwhile, the capture of electrons occur by interaction of active sites from solid with adsorbed molecules of oxygen to generate superoxide radical (Mueses, *et al.*, 2013).

In this mechanism, the molecular adsorption (of water and hydroxyl ions) is the limiting factor of the hydroxyl radical generation process. This is due because the adsorbed species are charge carriers for photogenerated holes (Linsebigler, *et al.*, 1995). Experiments have shown that the probability of organic compounds adsorption is low in comparison with the processes that involve water and hydroxyl ions (Fujishima, *et al.*, 2008). However, although we considered that adsorption of contaminant molecules is low compared with adsorbed water and hydroxyl ions, it is essential to quantify amount of molecules from organic substrate which are adsorbed on the semiconductor surface. This consideration is very important because the molecules on the catalyst surface involve the active sites available loss for activation via photoexcitation. In addition we require knowing the real initial concentration after dark phase and before of photodegradation; this prevents erroneous estimates in quantification of the mineralization global yields.

Conventionally, the quantification of adsorbed molecules is made using isotherms based on mathematical model of empirical expressions with adjustment parameters. An adsorption model represents the amount of adsorbent adhered to the material surface in function of the initial concentration (in adsorption/desorption equilibrium) or concentration in function of the time (in a kinetic model). The literature presents different expressions for isotherms, which vary according to the number of theoretical or empirical parameters. Some of these are: Langmuir (Gomes da Silva, 2003) (Giraldo, 2010), Freundlich (Yousef, *et al.*, 2011), Redlich-Peterson (Piccin, *et al.*, 2009), Tempkin (Khaled, *et al.*, 2009), Toth (Senthil Kumar, *et al.*, 2010) and Dubinin-

Radushkevich, among others. These equations can be used for prediction of fluid molecular adsorption over solid suspended particles inside of specific operational conditions (Allen, *et al.*, 2003).

The concentration of adsorbed reactant has a relation with the concentration fluid and depends of temperature, pH, surface semiconductor area and reactive nature. The temperature is kept constant during the measurements of global equilibrium concentration in the determination of an adsorption isotherm.

For description of heterogeneous photocatalysis molecular adsorption, different isotherm models have been used in different compounds: nitric oxide NO, TCE in gas phase, herbicides, cresols, chlorobenzene, chlorophenols, methyl and dimethyl amines and dyes such as auramine-O, carmine indigo and black remazol-5 (RB5), among others (Hunger, *et al.*, 2010) (Demeestere, *et al.*, 2004) (Kaneco, *et al.*, 2009) (Vulliet, *et al.*, 2003) (Pulido Melián, *et al.*, 2007) (Huang, *et al.*, 2008) (Pino & Encinas, 2012) (Helali, *et al.*, 2011) (Vasanth Kumar, *et al.*, 2007) (Barka, *et al.*, 2008). However, none of these models include molecular adsorption in the mathematical structure of the kinetic expression, thus the initial concentration quantification is not considered in the light phase. The main interest of this paper is to choose a semi-empirical mathematical model for description of the molecular adsorption for some organic pollutants in solution over TiO₂-P25 particles, and find the theoretical relation between the adsorption process and the heterogeneous photocatalytic mechanism based on hydroxyl radical attack.

2. Methodology

Selection of the adsorption isotherm model

Langmuir-Hinshelwood, Redlich-Peterson and Toth models have been considered to be more appropriate for description of the molecular adsorption step in heterogeneous photocatalysis. Theoretically, these models of equilibrium follow the molecular transport in the semiconductor/solution interface represented in Helmholtz layer

model. In general the three models are consistent with thermodynamic and dynamic of the interface. The main mechanism of these processes includes: *i*) Diffusion of key compound from bulk unto boundary of Gouy-Chapman layer, *ii*) molecular transport through Helmholtz layer, *iii*) molecular transport from boundary Helmholtz layer unto the catalyst surface and *iv*) adsorption over the surface (Linsebigler, *et al.*, 1995).

Langmuir-Hinshelwood model (L-H)

Langmuir-Hinshelwood model is commonly used to describe the heterogeneous photocatalytic kinetic (Kim, *et al.*, 2008) (Guillard, *et al.*, 2008) (Sagawe, *et al.*, 2005), although the mathematical development has been formulated to conventional catalytic processes and not by photocatalysis. The model is applied in adsorption process over flat surface (homogeneous) and it is thermodynamically consistent in the equilibrium of adsorption/desorption for the minimization of Gibbs energy in the process of adhesion between the molecule and the catalyst surface. The model follows the Henry's law to dilution conditions of adsorbate, but it has a deviation at high concentration. Although this is the main limitation on the kinetic of heterogeneous photocatalytic processes (illuminated phase), however, the molecular adsorption in dark phase is described satisfactorily.

The model shown in the eq. 1 was originally developed by Irving Langmuir to represent the gas-solid adsorption, but subsequently extended to solid-liquid systems. It was assumed that the surface containing the adsorption sites is perfectly flat without corrugations (homogeneous surface), the adsorbent is in a stable state, all sites are equivalent, adsorption occurs in a single layer (monolayer) and no interaction between adsorbate molecules and adjacent sites (Allen, *et al.*, 2004).

$$q_e = K_L \frac{a_L C_e}{1 + a_L C_e} \quad (1)$$

Where K_L and a_L are adsorption constant with units of (cm³/g) and (cm³/mg), respectively; q_e

is quantity of adsorbate in equilibrium by mass unit of adsorbent (mg/g) and C_e is the adsorbate concentration (mg/cm³).

Redlich-Peterson model

Redlich-Peterson model is also thermodynamically consistent in the phenomena of adsorption/desorption on the surface. The model represents a fictitious advantage in compared to Langmuir-Hinshelwood model. The predictions of the molecular adsorption can be effective both at high and low concentrations and therefore in principle corrects errors of Langmuir-Hinshelwood and Freundlich, however, the model has three parameters (see Eq. 2), one more that Langmuir-Hinshelwood, whereby it is not appropriate to establish a comparison numerically. The third parameter is an advantage in the adjustment of the experimental data but this parameter is not a representation of the physics the system. Redlich and Peterson introduced the three parameters to the isotherm for represent adsorption equilibriums in a wide range of concentrations (Pérez, *et al.*, 2007). The mathematical expression is:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \quad (2)$$

$$\beta \leq 1$$

Where K_R and a_R are adsorption constants with units of (cm³/g) and (cm³/mg); q_e is concentration of adsorbate in the equilibrium by mass unit of the adsorbent (mg/g); C_e is the initial concentration of adsorbate (mg/cm³) and β is adjustable parameter. This equation reduces to a lineal isotherm at low surface coverage, the Freundlich isotherm at a high adsorbate concentration and L-H isotherm if $\beta = 1$.

Toth model

Finally, Toth model is a combination of two models: one predicts well at low concentrations and another at high concentrations to obtain an acceptable adjustment in a wide range of concentrations. This model was obtained from

energy potential theory, which is applicable to the adsorption over heterogeneous surface and satisfies numerically the limitations present to high and low concentrations of the adsorbate. The model provides a good description for several systems with coverage sub-monolayer because consider the dependency of the monolayer with the temperature and introduce an empirical constant in function of the temperature of the system (Arias, *et al.*, 2009). The Eq. 3 describes the model:

$$q_e = \frac{K_T C_e}{[a_T + C_e]^t} \quad (3)$$

Where q_e is the final concentration in equilibrium per mass of adsorbent (mg/g), C_e is initial concentration of adsorbate (mg/cm³); K_T is a constant of the model in function of the temperature (mg/g), and a_T and t are adjustment parameters of the model, which do not have physical meaning.

Experiments

Materials and equipment

The tests were done using phenol (PH), 4-chlorophenol (4-CP) and dichloroacetic acid (DCA) from Merck® analytic grade as substrates of the system. Titanium dioxide (TiO₂-P25) from Degussa-Evonik (98%: 75% Anatase and 25% Rutile) was used as particle of adsorption. In addition HCl and NaOH from Merck® analytic grade were used to modify the pH in the solutions. The experimental data was obtained in a cylindrical glass vessel PYREX® inside of dark chamber to avoid contact between radiant light and catalyst particle. In addition the system was equipped with magnetic stirrer to guaranty the suspension of the particles (see Fig. 1). The analysis was done using a spectrophotometer SHIMADZU UV-1800.

Experimental procedures

The experimental test were done to ten values of initial concentration of the substrate (30, 50, 70, 90, 110, 130, 150, 180, 250, 300 mg/L) at pH 4, charge of catalyst of 0.1, 0.35, 0.5 and 1.0 g/L,



Figure 1. Experimental equipment scheme for molecular adsorption. 1: Cylindrical glass vessel PYREX®, 2: Magnetic stirrer, 3: Dark chamber.

and room temperature ($29 \pm 2^\circ\text{C}$) (Satuf *et al.*, 2005; Mueses *et al.*, 2013; Mueses & Machuca-Martínez, 2013). The spectrophotometer was calibrated following Beer-Lambert law with solutions of pure components each 10 mg/L in intervals between 20 and 300 mg/L. In a typical test for molecular adsorption we prepared the solution with the key compound, it was carried to previously defined operational conditions and it is stirred; subsequently the catalyst is added and the system keeps in stirrer during 12 hours. In the final time, the sample was filtered and it sent to analysis using the spectrophotometer (Mueses & Machuca-Martínez, 2013).

Parameter determination for molecular adsorption models

The model parameters were obtained using an optimization algorithm of nonlinear least squares coupled to modified Newton-Raphson algorithm with a damping parameter from Broyden (Mueses, *et al.*, 2013). The method involves the use of ordinary derivatives of objective functions for each parameter of the model. The objective functions are obtained from experimental data and mathematical structure of the models. In this

Table 2. Mathematical expressions used to parameters determination in molecular adsorption models.

Model	Parameter	Function
Langmuir-Hinshelwood	a_L	$f(a_L) = \sum_{i=1}^N \left[c_{e,i} \cdot \left(q_{e,i} - K_L \frac{a_L C_{e,i}}{1 + a_L C_{e,i}} \right) \frac{(1 - a_L C_{e,i})}{(1 + a_L C_{e,i})^2} \right] \approx 0$ (4)
	K_L	$f(K_L) = K_L - \sum_{i=1}^N q_{e,i} \left[\frac{C_{e,i}}{1 + a_L C_{e,i}} \right] / \sum_{i=1}^N \left[\frac{C_{e,i}}{1 + a_L C_{e,i}} \right]^2 \approx 0$ (5)
	K_R	$f(K_R) = K_R - \sum_{i=1}^N q_{e,i} \left[\frac{C_{e,i}}{1 + a_R C_{e,i}^\beta} \right] / \left[\frac{C_{e,i}}{1 + a_R C_{e,i}^\beta} \right]^2 \approx 0$ (6)
Redlich-Peterson	a_R	$f(a_R) = K_R - \sum_{i=1}^N q_{e,i} \left[\frac{C_{e,i}^{\beta+1}}{1 + a_R C_{e,i}^\beta} \right] / \sum_{i=1}^N \left[\frac{C_{e,i}^{\beta+2}}{1 + a_R C_{e,i}^\beta} \right]^3 \approx 0$ (7)
	β	$f(\beta) = \sum_{i=1}^N q_{e,i} \left[\frac{K_R C_{e,i}}{(1 + a_R C_{e,i}^\beta)} \right] \frac{\delta}{\delta \beta} \left(\frac{1}{1 + a_R C_{e,i}^\beta} \right) \approx 0$ (8)
Toth	K_T	$f(K_T) = K_T - \sum_{i=1}^N q_{e,i} \left[\frac{C_{e,i}}{(1 + a_L C_{e,i}^t)^{1/t}} \right] / \sum_{i=1}^N \frac{C_{e,i}^2}{(1 + a_L C_{e,i}^t)^{1/t}} \approx 0$ (9)
	a_T	$f(a_T) = \sum_{i=1}^N q_{e,i} \left[\frac{C_{e,i}}{(1 + a_L C_{e,i}^t)^{2/t}} \right] - K_T \sum_{i=1}^N \frac{C_{e,i}^2}{(1 + a_L C_{e,i}^t)^{3/t}} \approx 0$ (10)
	t	$f(t) = \sum_{i=1}^N C_{e,i} \left[q_{e,i} \frac{K_t C_{e,i}}{[a_T + C_{e,i}^t]^{1/t}} \right] \frac{\delta}{\delta t} \left(\frac{1}{[a_T + C_{e,i}^t]^{1/t}} \right) \approx 0$ (11)

paper the derivatives function were quantified by application of elementary calculus from Taylor series. In the Table 2 we showed the mathematical expressions for residual functions (objective functions) for each model.

This mathematical optimization is used because the linearization techniques do not generate appropriate adjustments; in general, the linearization techniques have good performance only if the experimental data are linear in the intervals where are applied. If the experimental data behaviors are of high order (high concentration for example) the adjustments are not correct. However a nonlinear model predicts more precisely the experimental data (Mueses *et al.*, 2013).

The system solution was done using the multivariable Newton-Raphson method. For each residual function, f_ψ , we established non-linear systems equations; for an iteration (m):

$$\sum_{k \neq R}^P \left(\frac{\delta f_\psi^{(m)}}{\delta f_k^{(m)}} \right) \cdot \Delta \psi_k^{(m)} + E_k(\psi_k^{(m)}) = 0 \quad (12)$$

In the equation, f_ψ corresponds to derivative function from residual discrepancies functions with respect to each parameter ψ in the iteration (m), $\Delta \psi_k^{(m)}$ is the solution for k parameter of the equation, $E_k(\psi_k^{(m)})$ is evaluation of residual functions, f_ψ in the iteration (m) and the summation corresponds to the Jacobian of residual functions. The lineal solution is:

$$\psi_k^{(m+1)} = \psi_k^{(m)} + S_k \Delta \psi_k^{(m)} \quad (13)$$

Here S_k is damping coefficient. In this paper we have considered a coefficient of Broyden type, which is generated by minimization of the Euclidian Norm obtained from the vector of residual discrepancies functions (Mueses & Machuca-Martínez, 2013). The value of S_k has two fundamental restrictions:

$$S_k = 1 \quad \text{si} \quad \eta < 1 \quad (14)$$

$$S_k = \frac{\sqrt{1 + 6\eta} - 1}{3\eta} \quad \text{si} \quad \eta < 1 \quad (15)$$

$$\eta = \frac{\sum_{k \neq R}^P [E_k(\psi^{(m+1)})]^2}{\sum_{k \neq R}^P [E_k(\psi^{(m)})]^2} \quad (16)$$

The use of the Broyden parameter S_k in this proposal allows continuous monitoring of the convergence path, besides having a direct mathematical functionality with the residual equations, reflecting high effective numerical stability and convergence to the solution of the system (Mueses & Machuca, 2013).

3. Results and discussion

The parameters obtained for each molecular adsorption model are presented in the Table 3. The observations suggest that Langmuir-Hinshelwood & Redlich-Peterson have global constants with orders of magnitude less than the adsorption constants. This phenomenon involves high adsorption of organic compounds over TiO_2 -P25 particles.

In the Figure 2 (a, b and c) we presented the experimental and simulation data obtained by application of the model and the optimization algorithm at optimal concentration of catalyst equal to 0.35 g/L of TiO_2 used in solar heterogeneous photocatalytic processes, according reports by Mueses *et al.* (2013) & Colina *et al.* (2009).

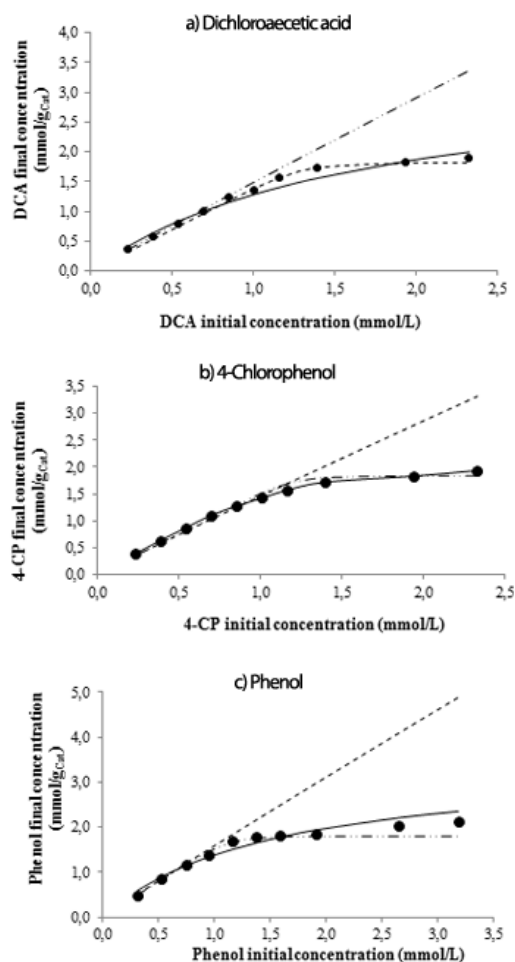


Figure 2. Experimental data (•) and simulations for molecular adsorption over TiO_2 -P25 particles: Langmuir-Hinshelwood (—), Toth (---) and Redlich-Petersen (.....)

In these results, the Langmuir-Hinshelwood isotherm and Toth described better the adsorption of the pollutants, but we considered that Langmuir-Hinshelwood is much appropriate because follows

Table 3. Parameters of the molecular adsorption models.

Model	Parameter	Values		
		DCA	4-CP	Phenol
Langmuir-Hinshelwood	a_L	0.5888	0.7824	0.6560
	K_L	3.4551	3.1299	3.4781
	K_R	2.1255	2.0185	2.0081
Redlich-Peterson	a_R	0.4321	0.3849	0.2674
	β	0.0976	0.1037	0.1259
	K_T	1.8171	1.8357	1.8016
Toth	a_T	13.0216	7.4869	2.6594
	t	9.455	10.6063	7.5592

the transport molecular mechanisms inside the interface semiconductor/solution represented in the layer Helmholtz model, moreover this is amply used in the reaction rate expression of the heterogeneous photocatalytic processes (Mueses *et al.*, 2013). Besides, Langmuir-Hinshelwood has one less parameter in comparison with Toth in the formulation.

Turchi & Ollis (1990) & Mueses *et al.* (2013) showed that the photocatalytic mechanism more accepted is based on hydroxyl radical attack in the interface semiconductor/solution (Helmholtz layer). The generated mathematical procedure for application of pseudo-stable state involves as result the inclusion of a mathematical term similar to Langmuir-Hinshelwood function, with a modification by effects of luminous flux and synergic contribution of quantum yield and LVRPA (Mueses, *et al.*, 2013). These results confirm the validity to use Langmuir-Hinshelwood model as a molecular adsorption mechanism for correct these effects over the kinetic of reaction rate in the photocatalysis process. This correction improves the description with respect to the organic compounds covering the free surface of the semiconductor and therefore improves the prediction of obtained experimental data, using only two parameters in a wide interval of the concentrations where photocatalysis is conventionally applied. The results support the validity of the Langmuir-Hinshelwood model in this processes type (Mueses & Machuca, 2013).

Furthermore, in the Figure 3 (a, b and c) we represented the performance of the molecular adsorption in function of the catalyst concentration both experimental data and the Langmuir (or Langmuir-Hinshelwood) model. We observed that the increase the catalyst concentration generates reductions on the molecular adsorption using a similar initial concentration of the pollutant and increases of the molecular adsorption with the increase of the substrate initial concentration. The predictions of the Langmuir-Hinshelwood model are effective for these operational conditions. It also is evidence a inflection point from the curve takes

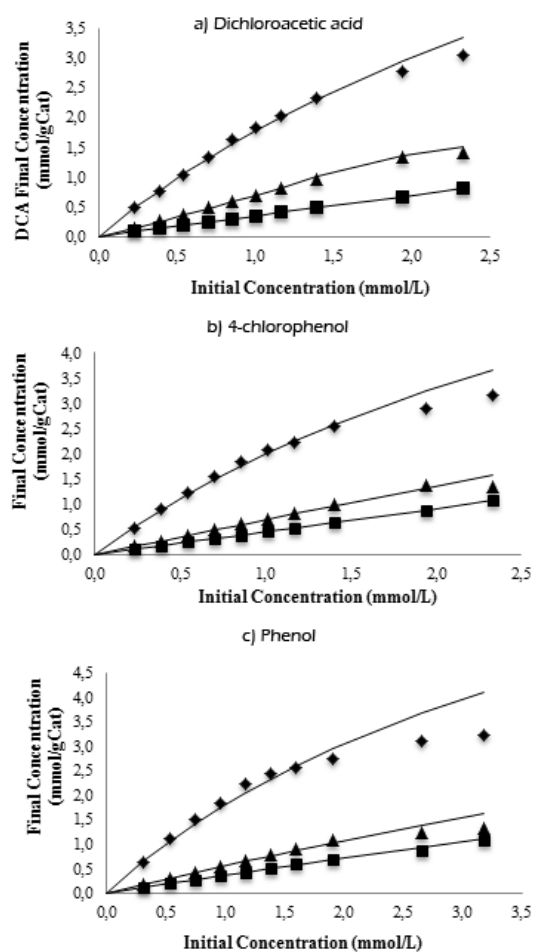


Figure 3. Experimental data and simulation (—) using L-H model of molecular adsorption to different concentration of TiO_2 -P25: 0.1 g/L (♦), 0.5 g/L (□) and 1.0 g/L (▲).

an asymptotic performance, which represents diminutions in the molecular adsorption due the active sites of the catalyst are occupied by water molecules, molecular oxygen, hydroxyl ions or organic compounds. These results are consistent with typical performance of L2 isotherms (Chen, *et al.*, 1995). The adsorptions of halogenated organic compounds over particles (e. g. DCA) are represented with L2 isotherm, which is concave in relation with solute concentration axes. For this performance is consider appropriate the adsorption isotherms of the Langmuir type, Langmuir of double site, Langmuir-Freundlich and Tóth, among other, whereby even though the Langmuir model has limitations frequently at high concentrations, in this case the adjustment is

effective. The adsorption at different values of the initial concentration of the catalyst showed that for high concentrations of TiO_2 the adsorption is unfavorable due to the agglomeration phenomena and this cause a reduction of specific surface available to the activation in a photoreaction (Bekkouche, *et al.*, 2004).

The obtained results showed that to concentrations less to 0.35 g/L, the adsorption presents asymptotic trends due to the saturation of active sites by high adsorption, while to concentration higher than 0.35 g/L, the performance of the curves presents lineal variation in function of catalyst concentration, even to the high initial concentration of substrate. These results support the saturation surface theory, which indicates that to high concentration of pollutants but low catalyst concentration the active sites are saturated; if now the catalyst concentration is increased these effects are not important due to the increase of available active sites. Finally, the results obtained in this research permit to confirm that Langmuir-Hinshelwood model can be used both molecular adsorption prediction in dark phase (before of photoreaction) and as a heterogeneous photocatalytic kinetic model using a modification with relation of photonic effect and quantum yield parameter (Mueses, *et al.*, 2013).

4. Conclusions

The selection of a molecular adsorption model was made from semi-theoretical models based on adsorption isotherms of L2 type. The evaluation and validation of the selection were done with experimental data of molecular adsorption for DCA, phenol and 4-chlorophenol over TiO_2 -P25 particles (Degussa-Evonik titanium dioxide) to different operational conditions. We obtained that the -Hinshelwood model is the better because the model permits the prediction of experimental data with high effectiveness in dark phase using only two adjustment parameters, in addition the theory selection involves the consistent with the molecular transport around of Helmholtz layer close to the surface.

5. Nomenclature

a_L	Langmuir-Hinshelwood constant	cm^3/mg
a_R	Redlich-Peterson isotherm constant	cm^3/mg
a_T	Toth isotherm constant	cm^3/mg
b	Toth isotherm parameter	
C_e	Equilibrium liquid-phase concentration	mg/cm^3
$E_k(\psi k^{(m)})$	residual function (dimensionless)	
f_ψ	derivative function (dimensionless)	
K_L	Langmuir-Hinshelwood constant	cm^3/mg
K_R	Redlich-Peterson isotherm constant	cm^3/mg
K_T	Toth isotherm constant	cm^3/mg
q_e	Measured contaminant equilibrium solid phase concentration	mg/cm^3
t	Toth isotherm potential parameter	

Greek Letters and special simbols

β	empirical constant for each adsorbate in Redlich-Peterson isotherm
k	parameter of Newton-Raphson algorithm
λ	dumping parameter of Broyden
ψ	parameter of residual function (dimensionless)

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Alcance y Política editorial de la revista

La revista Ingeniería y Competitividad es una publicación científica y tecnológica de la Facultad de Ingeniería de la Universidad del Valle, que tiene por objeto reportar avances de investigación en diversas ramas de la ingeniería (por ejemplo, ingeniería ambiental, de alimentos, civil, de computación, eléctrica, electrónica, estadística, industrial, de materiales, mecánica, química, sanitaria, de sistemas).

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La revista recibe contribuciones en los idiomas español, inglés o portugués. La revista acepta solamente tres tipos de trabajos de acuerdo con los criterios establecidos para la integración y clasificación de revistas de ciencia y tecnología colombianas en el Índice Bibliográfico Nacional Publindex de COLCIENCIAS:

Artículos de investigación científica o tecnológica: presentan resultados originales de investigación. Están típicamente integrados por cinco secciones: 1. Introducción, 2. Metodología, 3. Resultados y discusión, 4. Conclusiones, 5. Referencias bibliográficas.

Artículos de reflexión: presentan resultados de investigación sobre un tema específico desde la perspectiva analítica, interpretativa o crítica de los autores, recurriendo a fuentes bibliográficas originales.

Artículos de revisión: presentan el resultado de una revisión analítica de la literatura sobre un tema específico, sistematizando o integrando los resultados de investigaciones ya publicadas con el fin de dar cuenta del avance y las tendencias de desarrollo de ese tema. Incluyen una cuidadosa y amplia revisión bibliográfica.

En consecuencia, durante la fase de evaluación editorial inicial se rechazarán los siguientes tipos de trabajos: **artículos cortos** (en los cuales se presentan propuestas de investigación o resultados preliminares o parciales de un proyecto de investigación), **reportes de caso** (los cuales se limitan a presentar las experiencias técnicas y metodológicas asociadas al estudio de un caso específico), y **revisiones de tema** (revisiones bibliográficas sobre un tema específico que no incluyen aportes significativos por parte de los autores). Durante la fase final de diagramación del artículo (cuando se acepta y se envía a los autores en formato pdf para su revisión final), el autor podrá enviar al editor correcciones menores relacionadas con ortografía, párrafos repetidos, entre otras. Si el autor incluye algún párrafo, tabla, dato o gráfica, el artículo se someterá de nuevo al proceso de evaluación.

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Los trabajos se aceptan para publicación basándose en un proceso riguroso de revisión de su calidad académica. El Editor-Jefe, en conjunto con el miembro del Comité Editorial que está asociado al área de la ingeniería correspondiente al trabajo remitido, hace una primera evaluación, después de la cual, el trabajo se rechaza sin evaluación adicional o se acepta para evaluación de pares académicos (o árbitros). Los trabajos que se rechazan en esta primera etapa no son suficientemente originales, o tienen serias deficiencias en su estructura, o tienen una pobre redacción, o no cumplen con los requisitos de presentación de trabajos exigidos por la revista. Los trabajos que se aceptan en esta primera etapa son enviados a dos árbitros expertos en el área de conocimiento respectiva, cuyas identidades resultan desconocidas para los autores a través de todo el proceso de evaluación. Para asegurar la imparcialidad en la evaluación, las identidades de los autores también resultan desconocidas para los árbitros. O sea que el proceso de evaluación es doblemente ciego. Los árbitros disponen de un tiempo comprendido entre un mes y dos meses para remitir un concepto detallado sobre la organización y redacción del artículo, la originalidad y alcance del trabajo presentado, el planteamiento y justificación del problema abordado, la descripción de la metodología utilizada, la presentación y discusión de los resultados, la consistencia entre resultados y conclusiones, y la pertinencia y precisión de las referencias bibliográficas citadas.

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