Experimental and mathematical evaluation of molecular adsorption models for organic pollutants on TiO$_2$-P25 particles

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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 TiO$_2$-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: TiO$_2$-P25 photocatalyst, Organic compounds: DCA 4-Chlorophenol and Phenol, L2 isotherm.

Resumen
Se evaluaron modelos convencionales de adsorción molecular basados en isoterms del tipo L2 para compuestos orgánicos ácido dicloroacético, fenol y 4-clorofenol sobre partículas de TiO$_2$-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 fotocatálisis heterogénea. Los modelos fueron comparados con datos experimentales para determinar la isoterma más adecuada. El modelo L-H fue el más apropiado y los resultados fueron de alta efectividad en la predicción de los datos experimentales.

Palabras Clave: Fotocatalizador TiO$_2$-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) [Rj], 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>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>[ O^2_\text{III} + Ti^{IV} + H_2 \rightarrow O_\text{III} + Ti^{IV} \int OH^- ] M1a</td>
</tr>
<tr>
<td>Activation</td>
<td>[ Ti^{IV} + H_2O \rightarrow Ti^{IV} \int H_2O ] M1b</td>
</tr>
<tr>
<td></td>
<td>[ Site + R_i \rightarrow R_i\text{ads} ] M2</td>
</tr>
<tr>
<td></td>
<td>[ TiO_2 + h\nu \rightarrow e_{BC} + h_{BC} ] M3</td>
</tr>
<tr>
<td></td>
<td>[ OH^- + Ti^{IV} \leftrightarrow Ti^{IV} \int OH^- ] M4</td>
</tr>
<tr>
<td>Recombination</td>
<td>[ e^- + h^+ \rightarrow \text{heat} ] M5</td>
</tr>
<tr>
<td></td>
<td>[ Ti^{IV} \int OH^- + h^+ \rightarrow Ti^{IV} \int OH^- ] M6a</td>
</tr>
<tr>
<td>Electron-Holes capture</td>
<td>[ Ti^{IV} \int H_2O + h^+ \rightarrow Ti^{IV} \int OH^- + H^+ ] M6b</td>
</tr>
<tr>
<td></td>
<td>[ R_{i,\text{ads}} + h^+ \rightarrow R_{i,\text{ads}}^{+} ] M7</td>
</tr>
<tr>
<td></td>
<td>[ Ti^{IV} + e^- \rightarrow Ti^{III} ] M8a</td>
</tr>
<tr>
<td></td>
<td>[ Ti^{III} + O_2 \rightarrow Ti^{IV} \int O_\text{II} ] M8b</td>
</tr>
<tr>
<td></td>
<td>[ Ti^{IV} \int OH^- + R_{i,\text{ads}} \rightarrow Ti^{IV} + R_{j,\text{ads}} ] M9a</td>
</tr>
<tr>
<td>Hydroxyl radical attack</td>
<td>[ OH^- + R_{i,\text{ads}} \rightarrow Ti^{IV} + R_{j,\text{ads}} ] M9b</td>
</tr>
<tr>
<td></td>
<td>[ Ti^{IV} \int OH^- + R_i \rightarrow Ti^{IV} + R_j ] M10a</td>
</tr>
<tr>
<td></td>
<td>[ OH^- + R_i \rightarrow Ti^{IV} + R_j ] M10b</td>
</tr>
</tbody>
</table>
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 TiO$_2$-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. Theorically, 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).

\[
q_e = K_L \frac{a_L C_i}{1 + a_L C_i} \tag{1}
\]

Where \(K_L\) and \(a_L\) are adsorption constant with units of (cm\(^3\)/g) and (cm\(^3\)/mg), respectively; \(q_e\) is quantity of adsorbate in equilibrium by mass unit of adsorbent (mg/g) and \(C_i\) is the adsorbate concentration (mg/cm\(^3\)).

**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:

\[
q_e = \frac{K_R C_i}{1 + a_R C_i} + \frac{\beta K_R C_i}{1 + \beta a_R C_i} \tag{2}
\]

Where \(K_R\) and \(a_R\) are adsorption constants with units of (cm\(^3\)/g) and (cm\(^3\)/mg); \(q_e\) is concentration of adsorbate in the equilibrium by mass unit of the adsorbent (mg/g); \(C_i\) is the initial concentration of adsorbate (mg/cm\(^3\)) and \(\beta\) 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:

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

Where \( q_e \) is the final concentration in equilibrium per mass of adsorbent (mg/g), \( C_e \) is initial concentration of adsorbate (mg/cm\(^3\)); \( K_T \) 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 (TiO\(_2\)-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, and room temperature (29 ± 2°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
The system solution was done using the multivariable Newton-Raphson method. For each residual function, \( f_a \), we established non-linear systems equations; for an iteration \( (m) \):

\[
\sum_{k \neq R}^p \left( \frac{\delta f_a^{(m)}}{\delta f_k^{(m)}} \right) \cdot \Delta \psi_k^{(m)} + E_i(\psi_k^{(m)}) = 0
\]

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

\[
\psi_k^{(m+1)} = \psi_k^{(m)} + S_i \Delta \psi_k^{(m)}
\]

Here \( S_i \) 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:

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

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir-Hinshelwood</td>
<td>( a_L )</td>
<td>[ f(a_L) = \sum_{i=1}^{N} \left[ c_{c,i} \left( q_{c,i} - K_L \frac{a_L C_{c,i}}{1 + a_L C_{c,i}} \right) \right] \approx 0 ]</td>
</tr>
<tr>
<td></td>
<td>( K_L )</td>
<td>[ f(K_L) = \sum_{i=1}^{N} \left[ \frac{c_{c,i}}{1 + a_L C_{c,i}} \right] / \sum_{i=1}^{N} \left[ \frac{c_{c,i}}{1 + a_L C_{c,i}} \right] \approx 0 ]</td>
</tr>
<tr>
<td></td>
<td>( K_R )</td>
<td>[ f(K_R) = \sum_{i=1}^{N} \left[ \frac{c_{c,i}}{1 + a_R C_{c,i}^R} \right] / \sum_{i=1}^{N} \left[ \frac{c_{c,i}}{1 + a_R C_{c,i}^R} \right] \approx 0 ]</td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td>( a_R )</td>
<td>[ f(a_R) = \sum_{i=1}^{N} \left[ \frac{c_{c,i}}{1 + a_R C_{c,i}^R} \right] / \sum_{i=1}^{N} \left[ \frac{c_{c,i}}{1 + a_R C_{c,i}^R} \right] \approx 0 ]</td>
</tr>
<tr>
<td></td>
<td>( \beta )</td>
<td>[ f(\beta) = \sum_{i=1}^{N} \left[ \frac{K_R C_{c,i}}{(1 + a_R C_{c,i}^R)^2} \right] - K_i \sum_{i=1}^{N} \left[ \frac{C_{c,i}^R}{(1 + a_R C_{c,i}^R)^{1/2}} \right] \approx 0 ]</td>
</tr>
<tr>
<td>Toth</td>
<td>( a_T )</td>
<td>[ f(a_T) = \sum_{i=1}^{N} \left[ \frac{C_{c,i}}{(1 + a_L C_{c,i}^T)^{1/2}} \right] - K_i \sum_{i=1}^{N} \left[ \frac{C_{c,i}^T}{(1 + a_L C_{c,i}^T)^{2/3}} \right] \approx 0 ]</td>
</tr>
<tr>
<td></td>
<td>( t )</td>
<td>[ f(t) = \sum_{i=1}^{N} \left[ \frac{K C_{c,i}}{(a_T + C_{c,i})^{1/2}} \right] - K_i \sum_{i=1}^{N} \left[ \frac{1}{(a_T + C_{c,i})^{1/2}} \right] \approx 0 ]</td>
</tr>
</tbody>
</table>
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).

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

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

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

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

Table 3. Parameters of the molecular adsorption models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>DCA</th>
<th>4-CP</th>
<th>Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir-Hinshelwood</td>
<td>$a_1$</td>
<td>0.5888</td>
<td>0.7824</td>
<td>0.6560</td>
</tr>
<tr>
<td></td>
<td>$K_L$</td>
<td>3.4551</td>
<td>3.1299</td>
<td>3.4781</td>
</tr>
<tr>
<td></td>
<td>$K_R$</td>
<td>2.1255</td>
<td>2.0185</td>
<td>2.0081</td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td>$a_R$</td>
<td>0.4321</td>
<td>0.3849</td>
<td>0.2674</td>
</tr>
<tr>
<td></td>
<td>$\beta$</td>
<td>0.0976</td>
<td>0.1037</td>
<td>0.1259</td>
</tr>
<tr>
<td></td>
<td>$K_T$</td>
<td>1.8171</td>
<td>1.8357</td>
<td>1.8016</td>
</tr>
<tr>
<td>Toth</td>
<td>$a_T$</td>
<td>13.0216</td>
<td>7.4869</td>
<td>2.6594</td>
</tr>
<tr>
<td></td>
<td>$t$</td>
<td>9.455</td>
<td>10.6063</td>
<td>7.5592</td>
</tr>
</tbody>
</table>
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 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 TiO2-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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_L$</td>
<td>Langmuir-Hinshelwood constant</td>
</tr>
<tr>
<td>$a_R$</td>
<td>Redlich-Peterson isotherm constant</td>
</tr>
<tr>
<td>$a_T$</td>
<td>Toth isotherm constant</td>
</tr>
<tr>
<td>$b$</td>
<td>Toth isotherm parameter</td>
</tr>
<tr>
<td>$C_e$</td>
<td>Equilibrium liquid-phase concentration</td>
</tr>
<tr>
<td>$E_k(ψ)^{(m)}$</td>
<td>residual function (dimensionless)</td>
</tr>
<tr>
<td>$f_ψ$</td>
<td>derivative function (dimensionless)</td>
</tr>
<tr>
<td>$K_L$</td>
<td>Langmuir-Hinshelwood constant</td>
</tr>
<tr>
<td>$K_R$</td>
<td>Redlich-Peterson isotherm constant</td>
</tr>
<tr>
<td>$K_T$</td>
<td>Toth isotherm constant</td>
</tr>
<tr>
<td>$q_e$</td>
<td>Measured contaminant equilibrium solid phase concentration</td>
</tr>
<tr>
<td>$t$</td>
<td>Toth isotherm potential parameter</td>
</tr>
</tbody>
</table>

Greek Letters and special symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$β$</td>
<td>empirical constant for each adsorbate in Redlich-Peterson isotherm</td>
</tr>
<tr>
<td>$k$</td>
<td>parameter of Newton-Raphson algorithm</td>
</tr>
<tr>
<td>$λ$</td>
<td>dumping parameter of Broyden</td>
</tr>
<tr>
<td>$ψ$</td>
<td>parameter of residual function (dimensionless)</td>
</tr>
</tbody>
</table>

6. Acknowledgments

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7. References

for basic dye adsorption by kudzu. *Bioresource Technology* 88, 143-152.


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