

## Some remarks on the Langmuir–Hinshelwood kinetics

J. Alvarez-Ramirez<sup>1,2</sup> · R. Femat<sup>2</sup> · M. Meraz<sup>3</sup> ·  
C. Ibarra-Valdez<sup>4</sup>

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**Abstract** This work considered the Langmuir–Hinshelwood (LH) scheme for a single reactant. In a first step, the validity of the quasi-steady state approximation (QSSA) was revised in terms of nonlinear relaxation processes. It was found that the LH equation obtained from the QSSA is not valid most of the times, except for example in the case of high reactant concentrations when the relaxation time is small enough to reduce the order of the underlying system of differential equations. Subsequently, the observability properties of the LH equations were studied in order to find that the dynamical behavior of the adsorption complex can be reconstructed from measurements of the reactant trajectory. Finally, the estimation problem of the kinetic parameters based solely on the reactant concentration behavior was considered. It is then shown that the full set of kinetic parameters can be estimated from a single reactant depletion curve by solving a least-squares problem for the complete LH scheme. Numerical results were used to illustrate the findings of this work.

**Keywords** Langmuir–Hinshelwood · Quasi-steady state approximation · Observability · Parameter estimation

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✉ J. Alvarez-Ramirez  
jjar@xanum.uam.mx

<sup>1</sup> Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-534, 09340 Iztapalapa, D.F., Mexico

<sup>2</sup> División de Matemáticas Aplicadas, IPICyT, Camino a la Presa de San José 2055, Lomas 4a Secc, 78290 San Luis Potosí, S.L.P., Mexico

<sup>3</sup> Departamento de Biotecnología, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-535, 09340 Iztapalapa, D.F., Mexico

<sup>4</sup> Departamento de Matemáticas, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-535, 09340 Iztapalapa, D.F., Mexico

## 1 Introduction

The Langmuir–Hinshelwood (LH) model is widely used to describe the kinetics of heterogeneous catalytic processes. In its simplest form, the LH reaction scheme considers a reaction step where a reactant  $R$  is reversibly adsorbed on an active site  $S$  to form an adsorption complex  $C$ . In a second step, the adsorption complex can be transformed irreversibly into a product  $P$  and the active site is free to adsorb another reactant molecule. The irreversible version of this adsorption-reaction process can be schematically described as follows:



Here,  $k_a$ ,  $k_d$  and  $k_{cat}$  are the respective constants of the adsorption, desorption and reaction steps. When the heterogeneous reaction takes place in a closed system, the LH equations can be described in textbooks as follows [1,2]. The global reaction rate is expressed as

$$\frac{dP}{dt} = k_{cat}C \quad (2)$$

Commonly, the above equation is expressed in terms of the surface coverage fraction  $\theta = C/S_T$ , where  $S_T$  is the total number of sites (occupied or not). That is,

$$\frac{dP}{dt} = k_{cat}S_T\theta \quad (3)$$

On the other hand, the balance of occupied sites is given by

$$\begin{aligned} \frac{dC}{dt} &= k_a R(S_T - C) - (k_d + k_{cat})C \\ &= S_T [k_a R(1 - \theta) - (k_d + k_{cat})\theta] \end{aligned} \quad (4)$$

In principle, one can use Eqs. (2) and (4) to analyze the behavior of heterogeneous adsorption-reaction processes. However, the analysis is hampered by the lack of measurements of the adsorption complex concentration  $C$ . In typical experimental assays, while the behavior of the reactant concentration  $R(t)$  is available for measurements, the adsorption complex concentration  $C(t)$  is not. An approach to remedy this problem is to eliminate the adsorption complex concentration in Eq. (2). The traditional approach to achieve such task is based on a quasi-steady-state approximation (QSSA) for the adsorption complex concentration, which states that intermediate adsorption complex concentration does not change on the time-scale of product formation. This assumption implies that  $dC/dt \approx 0$  or, equivalently,  $k_a(S_T - C)R - (k_d + k_{cat})C \approx 0$ . Under such assumption, one can obtain the approximation  $C \approx k_a S_0 R / (k_d + k_{cat} + k_a R)$ , which can be used in Eq. (2) to obtain the standard LH reaction rate:

$$r_P \equiv \frac{dP}{dt} = \frac{k_{cat}S_T R}{K_{LH} + R} \quad (5)$$

Here, the LH constant  $K_{LH}$  is given by

$$K_{LH} = \frac{k_d + k_{cat}}{k_a} \quad (6)$$

The LH reaction rate given by Eq. (5) has two reaction order regimes: (a) if the reactant concentration is in excess with respect to the LH constant (*i.e.*,  $R \gg K_{LH}$ ), the reaction rate can be approximated by a zero-order kinetics of the form  $r_R \approx -k_{cat}S_T/K_{LH}$ , and (b) if the reactant concentration is in defect, the reaction rate can be approximated by a first-order kinetics of the form  $r_R \approx -(k_{cat}/K_{LH})S_TR$ .

Despite the widespread usage of the LH equation, there is a lack of detailed analysis on its limitations related to the QSSA. For instance, it has been noticed that the approximation of the LH kinetics to zero-order for heterogeneous catalyst is inappropriate [3]. Contrary to this claim, it was shown that the zero-order regimen can be justified only over a limited set of experimental data [4]. However, the complete LH equation should be used over wide ranges of reactant concentrations. It was also found that the approximation of the LH kinetics as a first-order reaction for the photocatalytic degradation of Auramine O aqueous solutions by ZnO catalyst can lead to inaccurate results [5]. It was shown that an apparent synergy between activated carbon and TiO<sub>2</sub> particles in heterogeneous photocatalytic process arises from the erroneous use of the first-order form of the LH equation [6]. Furthermore, results showed that the first-order and power-law kinetics are unable to provide a good fit to the experimental data for low reactant concentration values.

The aim of this work is to establish conditions for the validity of the QSSA used in the derivation of the standard LH equation. To this end, the system of differential equations derived from the LH reaction is reduced to a second-order differential equation for reactant concentration dynamics. Described in terms of the reaction rate, the equation obtained has the structure of a first-order relaxation process with asymptotic convergence to the standard LH equation. It is shown that this form of the differential Langmuir–Hinshelwood can be reduced to the traditional expression when the relaxation time is sufficiently small. Based on observability properties for the adsorption complex concentration, the full set of differential equations from the LH scheme was used to fit appropriately the experimental data sets extracted from the literature.

## 2 Derivation of the differential equations for the LH reaction scheme

The QSSA is an important step to obtain the LH equation. The key assumption is to neglect the time derivative  $dC/dt$  from the complex dynamics in Eq. (4) to obtain an easy solution of the complex concentration  $C$  in terms of the reactant concentration  $R$ . Namely,  $C \approx k_a S_T / (k_d + k_{cat} + k_a R)$ . Also, the QSSA implies the following equivalence between reactant and product reaction rates:

$$r_P = -r_R \quad (7)$$

so that, at any given time, the global reaction rate is indistinctly given in terms of the reactant or the product dynamics. However, the QSSA relies on heuristic arguments. The problem is the lack of guarantee that the dynamical effects induced by the term

$dC/dt$  can be neglected. In this way, a general analysis of the LH reaction scheme should consider that the dynamics of the adsorption complex  $C$  cannot be neglected. That is, the adsorption step is not equilibrated with the desorption step. As a consequence, the identity given by Eq. (7) is not longer satisfied. That is, the general analysis of the LH reaction scheme should consider the complete set of variables; namely, reactant concentration  $R$ , surface coverage fraction  $\theta$ , and product concentration  $P$ . Before proceeding to the analysis of the LH scheme and the conditions under which the QSSA can be satisfied, let us make a key observation concerning the physical consistency of Eqs. (2) and (4). In terms of the surface coverage fraction  $\theta$ , Eq. (2) can be written as

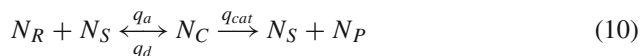
$$\frac{dP}{dt} = k_{cat} S_T \theta \quad (8)$$

On the other hand, the dynamical behavior of the surface coverage fraction is given by

$$\frac{d\theta}{dt} = k_a R(1 - \theta) - (k_d + k_{cat})\theta \quad (9)$$

The involved physical units are given as follows:  $\theta$  [=] dimensionless,  $P$  [=]  $\text{mol cm}^{-3}$ ,  $S_T$  [=]  $\text{sites cm}^{-2}$ . This would imply that  $k_{cat}$  [=]  $\text{mol s}^{-1} \text{cm}^{-1} \text{sites}^{-1}$  in Eq. (8), and  $k_{cat}$  [=]  $\text{s}^{-1}$  in Eq. (9). Obviously, the same physical units (actually,  $\text{s}^{-1}$ ) should be used in both differential equations. The origin of this physical inconsistency relies on the use of two different bases to express concentrations. While reactant and product concentrations are expressed on a volumetric basis (i.e.,  $\text{mol cm}^{-3}$ ), sites and complex adsorption concentrations are expressed on a superficial basis. To overcome this inconsistency, a derivation of the differential equations for the LH equations will be given below.

Consider a closed system of volume  $V$  with an active surface of area  $A$ . At time  $t$ , the volume  $V$  contains  $N_R(t)$  and  $N_P(t)$  molecules of reactant and product, respectively. On the other hand, the area  $A$  contains  $N_T$  adsorption sites of which  $N_C(t)$  are occupied by the adsorbed reactant (i.e., adsorption complex) and  $N_S(t)$  are unoccupied active sites. By assuming no deactivation, one has that  $N_S(t) + N_C(t) = N_T$ , for all  $t \geq 0$ . It can be also assumed that one active site on the surface can be occupied only by one reactant molecule, so that one can take a molecular basis for units of active sites. The LH chemical reaction scheme for a single reactant is then the following:



where the parameters  $q_a$ ,  $q_d$  and  $q_{cat}$  can be seen as probabilities of adsorption, desorption and reaction, respectively. The physical units of the parameters are given by  $q_a$  [=]  $\text{mol}^{-1} \text{s}^{-1}$ ,  $q_d$  [=]  $\text{s}^{-1}$  and  $q_{cat}$  [=]  $\text{s}^{-1}$ . Following the Gillespie's approach [7] to obtain the master equation for the LH scheme, one obtains the following system of differential equations:

$$\begin{aligned} \frac{dN_S}{dt} &= -q_a N_S N_R + (q_d + q_{cat}) N_C \\ \frac{dN_R}{dt} &= -q_a N_S N_R + q_d N_C \end{aligned}$$

$$\begin{aligned}\frac{dN_C}{dt} &= q_a N_S N_R - (q_d + q_{cat}) N_C \\ \frac{dN_P}{dt} &= q_{cat} N_C\end{aligned}\quad (11)$$

with initial conditions given by  $N_S(0) = N_{S,0}$ ,  $N_R(0) = N_{R,0}$ ,  $N_C(0) = N_{C,0}$  and  $N_P(0) = N_{P,0}$ . In general, one can take  $N_{P,0} = 0$ . For all  $t \geq 0$ , the following balance invariants are satisfied for system (11):

$$\begin{aligned}N_S(t) + N_C(t) &= N_T \\ N_R(t) + N_C(t) + N_P(t) &= N_{R,0}\end{aligned}\quad (12)$$

Since  $N_S(t) = N_T - N_C(t)$  and  $N_P(t) = N_{R,0} - N_C(t) - N_R(t)$ , system (11) can be expressed in terms of the dynamics of  $N_R(t)$  and  $N_C(t)$  as follows:

$$\begin{aligned}\frac{dN_R}{dt} &= -q_a (N_T - N_C) N_R + q_d N_C \\ \frac{dN_C}{dt} &= q_a (N_T - N_C) N_R - (q_d + q_{cat}) N_C\end{aligned}\quad (13)$$

That is, given the reactant  $N_R(t)$  and the adsorption complex  $N_C(t)$  dynamics, then the active sites  $N_S(t)$  and product  $N_P(t)$  dynamics can be obtained from the two balances given by Eq. (12).

The system of differential equation (13) is given in terms of extensive variables (i.e., number of molecules). In order to translate these expressions into intensive variables (i.e., concentrations), one should consider that the chemical species are distributed in two different topological regions. The reactant concentration should be given on a volumetric basis, while the adsorption complex dynamics on a superficial basis. By some abuse of notation, take the reactant and product concentrations as  $R = N_R/V$  and  $P = N_P/V$ , respectively. Similarly, the concentration of active sites and adsorption complex are expressed as  $S = N_S/A$  and  $C = N_C/A$ , respectively. By using concentrations instead number of molecules, the system of differential equations (13) can be expressed as follows:

$$\begin{aligned}\frac{dR}{dt} &= -(Aq_a) (S_T - C) R + q_d (A/V) C \\ \frac{dC}{dt} &= (V/A) [(Aq_a) (V/A) (S_T - C) R - (q_d + q_{cat}) (A/V) C]\end{aligned}\quad (14)$$

where  $S_T = N_T/A$ . The quantity  $\alpha = A/V$  corresponds to the specific area of the heterogeneous reacting system. On the other hand, one can take the standard kinetics parameters as follows:  $\kappa_a \equiv Aq_a$ ,  $\kappa_d \equiv (A/V)q_d$  and  $\kappa_{cat} \equiv (A/V)q_{cat}$ . Therefore, the differential equations (14) can be written as

$$\begin{aligned}\frac{dR}{dt} &= -\kappa_a (S_T - C) R + \kappa_d C \\ \frac{dC}{dt} &= \alpha^{-1} [\kappa_a (S_T - C) R - (\kappa_d + \kappa_{cat}) C]\end{aligned}\quad (15)$$

Also, the dynamical behavior of the product concentration is governed by

$$\frac{dP}{dt} = k_{cat}C \quad (16)$$

Next, introduce the following set of kinetic parameters:  $k_a = \kappa_a/\alpha$ ,  $k_d = \kappa_d/\alpha$  and  $k_{cat} = \kappa_{cat}/\alpha$ . In terms of the surface coverage fraction  $\theta$ , Eqs. (15) and (16) can be described as

$$\begin{aligned} \frac{dR}{dt} &= \Sigma_T [-k_a(1-\theta)R + k_d\theta] \\ \frac{d\theta}{dt} &= k_a(1-\theta)R - (k_d + k_{cat})\theta \\ \frac{dP}{dt} &= \Sigma_T k_{cat}\theta \end{aligned} \quad (17)$$

where  $\Sigma_T = \alpha S_T$  is the total number of sites on a volumetric basis (i.e.,  $\Sigma_T$  [=] sites  $\text{cm}^{-3}$ ). The physical units of the new set of kinetic parameters are  $k_a$  [=]  $\text{cm}^{-3} \text{mol}^{-1} \text{s}^{-1}$ ,  $k_d$  [=]  $\text{s}^{-1}$  and  $k_{cat}$  [=]  $\text{s}^{-1}$ . Actually, these are the physical units used in textbooks [1,2]. In fact, desorption and reaction steps involve only one chemical species (adsorption complex), so that in terms of the law of mass action they correspond to first-order kinetics. On the other hand, the system of differential equation (17) has the following advantages: a)  $\theta \in [0, 1]$ , and b) the parameter  $\Sigma_T$  is of the same order of magnitude of the reactant  $R$  and product  $P$  concentrations. Furthermore, it is noted that the QSSA implies that  $d\theta/dt \approx 0$ , so that  $\theta \approx k_a R / (k_a R + k_d + k_{cat})$ . In this case, the product reaction rate is given by

$$\frac{dP}{dt} = \Sigma_T \frac{k_{cat}R\theta}{K_{LH} + R} \quad (18)$$

This expression is similar to Eq. (5), except by the factor  $\Sigma_T$ . It should be emphasized that the factor  $\Sigma_T$  is necessary in Eq. (18) to guarantee the dimensional consistency of parameters and variables. The system of differential equations (17) will be the departing point for testing the validity of the QSSA in the LH reaction scheme.

### 3 Validity of the QSSA

#### 3.1 Product concentration dynamics

Next, expressions for the reaction rate depending only on accessible measurements (i.e., reactant and product concentration) will be obtained by means of simple algebraic manipulations. The equality  $\Sigma_T k_{cat}\theta = dP/dt$  implies that  $d^2P/dt^2 = \Sigma_T k_{cat}d\theta/dt$ . One can use the balance of the adsorption complex in the above equality to obtain

$$\frac{d^2P}{dt^2} = k_{cat}\Sigma_T [k_a(1-\theta)R - (k_d + k_{cat})\theta]R \quad (19)$$

Using the fact that  $\Sigma_T k_{cat} \theta = dP/dt$ , Eq. (19) can be rewritten as

$$\frac{d^2 P}{dt^2} + (k_d + k_{cat} + k_a R) \frac{dP}{dt} = \Sigma_T k_{cat} k_a R \quad (20)$$

The result expressed by Eq. (20) shows that the product behavior is governed by a second-order differential equation that depends only on reactant and product concentrations. In fact, Eq. (20) is an exact representation of the product dynamics that does not depend on the complex concentration. This second-order differential representation indicates that the product dynamics contains two concentration-dependent relaxation times associated with the adsorption and the reaction steps.

### 3.2 Reactant concentration dynamics

The concentration of the complex intermediate can be also eliminated from the reactant concentration behavior using simple algebraic manipulations. From Eq. (17), the second derivative of the reactant concentration is given by

$$\frac{d^2 R}{dt^2} = \Sigma_T \left[ -k_a(1 - \theta) \frac{dR}{dt} + (k_a R + k_d) \frac{d\theta}{dt} \right] \quad (21)$$

Since  $N_P(t) = N_T - N_C(t) - N_R(t)$ , one has that  $\Sigma_T \theta = \Sigma_T - R - P$  and

$$\Sigma_T \frac{d\theta}{dt} = -\frac{dR}{dt} - \frac{dP}{dt} \quad (22)$$

This expression can be used in Eq. (21) to obtain

$$\frac{d^2 R}{dt^2} = -\Sigma_T k_a (1 - \theta) \frac{dR}{dt} - (k_a R + k_d) \left( \frac{dR}{dt} + \frac{dP}{dt} \right) \quad (23)$$

On the other hand, one can use the equality  $\Sigma_T k_{cat} \theta = dP/dt$  in Eq. (23) to obtain the following expression:

$$\frac{d^2 R}{dt^2} + \left( k_a \Sigma_T + k_a R + k_d - \left( \frac{k_a}{k_{cat}} \right) \frac{dP}{dt} \right) \frac{dR}{dt} = - (k_a R + k_d) \frac{dP}{dt} \quad (24)$$

Eq. (24) is a nonlinear second-order differential equation that governs the dynamics of the reactant concentration. As required, Eq. (24) depends on the concentrations of reactant and the product, but not on the concentration of the adsorption complex.

### 3.3 Quasi-steady-state approximation

An interesting question related to the QSSA is to establish conditions under which the differential LH (dLH) given by Eqs. (18) and (22) can be approximated by the standard form of the LH equation. To address this issue, let  $r_P = dP/dt$  be the rate of product formation. One has that Eq. (20) can be written as

$$\tau_P(R) \frac{dr_P}{dt} + r_P = \frac{k_{cat} \Sigma_T R}{K_{LH} + R} \quad (25)$$

where the LH constant  $K_{LH}$  is given by Eq. (6), and  $\tau_P(R)$  is given by

$$\tau_P(R) = \frac{1}{k_d + k_{cat} + k_a R} \quad (26)$$

The function  $\tau_P(R)$  can be interpreted as a reactant-dependent relaxation time, which corresponds to the relaxation characteristic time scale of the first-order differential process  $\tau_P(R) \frac{dr_P}{dt} + r_P$ . On the other hand, if  $r_R \equiv dR/dt$  denotes the reactant reaction rate, then from Eq. (24) one can get

$$\tau_R(R, P) \frac{dr_R}{dt} + r_R = -\frac{(k_a R + k_d) r_P}{k_a \Sigma_T + k_a R + k_d - (k_a/k_{cat}) r_P} \quad (27)$$

Here, the relaxation time  $\tau_R(R, P)$  is given by

$$\tau_R(R, P) = \frac{1}{k_a \Sigma_T + k_a R + k_d - (k_a/k_{cat}) r_P} \quad (28)$$

An interesting question is to determine the conditions required to neglect the dynamical effects in the reaction rate expressions (25) and (27). In turn, this would reduce the above first-order differential equations to algebraic relationships between concentration and reaction rates. The following limit cases can be considered:

- *Excess of reactant concentration* Assume that the reactant concentration is in large excess with respect to the LH constant  $K_{LH}$  (i.e.,  $R \gg K_{LH}$ ). Recall that  $K_{LH} = (k_d + k_{cat})/k_a$ . This implies that  $\tau_P(R) \ll 1$ , by virtue of which Eq. (25) can be approximated by

$$r_P \approx k_{cat} \Sigma_T \quad (29)$$

That is, the product reaction rate can be approximated by zero-order kinetics under excess of reactant concentration. Note that Eq. (29) corresponds to the standard LH given by Eq. (5) for  $R \gg K_{LH}$ . It can be concluded that the differential form of the LH kinetics given by Eq. (20) can be approximated by the standard LH kinetics (5) when the reactant concentration is in excess with respect to the LH constant  $K_{LH}$  (i.e., the QSSA is valid). This result is in agreement with the findings by Murzin [4] who showed that the zero-order LH kinetics corresponds to complete saturation of the active sites by the reactant. In turn, saturation can be achieved by an excess of the reactant concentration. Regarding the reactant transformation kinetics, the condition  $\tau_R(R, P) \ll 1$  and the approximation (18) lead to the approximations

$$\begin{aligned} r_R &= -\frac{(k_a R + k_d) r_P}{k_a \Sigma_T + k_a R + k_d - (k_a/k_{cat}) r_P} \\ r_A &\approx -\frac{(k_a R + k_d) r_{P,SLH}}{k_a \Sigma_T + k_a R + k_d - (k_d/k_{cat}) r_{P,SLH}} \\ &= -k_{cat} S_T \end{aligned} \quad (30)$$



where  $r_{P,SLH}$  is the standard LH reaction rate given by Eq. (5). Interestingly, under reactant concentration excess the corresponding kinetics is also reduced to the standard LH kinetics.

- *Deficit of reactant concentration* If  $R \ll K_{LH}$ , the relaxation time can be approximated by  $\tau_P(R) \approx \frac{1}{k_a + k_{cat}}$ , so that Eq. (20) can be expressed as

$$\frac{dr_P}{dt} + (k_a + k_{cat})r_P = k_{cat}k_d\Sigma_T R \quad (31)$$

Eq. (31) is a linear differential equation with constant relaxation time and asymptotic limit  $r_P \rightarrow (k_{cat}/K_{LH})\Sigma_T R$ . In turn, this limit corresponds to the standard LH kinetics (see Eq. 17) under the assumption that  $R \ll K_{LH}$ . However, Eq. (31) states that the QSSA cannot be justified for the case of deficit of the reactant concentration since the dynamical effect reflected by the derivative  $dr_P/dt$  cannot be neglected.

- *Excess of active sites* Assume that  $\Sigma_T \gg R$ . This condition does not affect the relaxation time of the product dynamics in Eq. (25), so that the QSSA cannot be used for excess of active sites concentration. Regarding the reactant kinetics, one has that

$$\tau_R(R, P) \approx \frac{1}{k_a\Sigma_T + k_d - (k_a/k_{cat})r_P} \quad (32)$$

so then

$$\frac{dr_R}{dt} + (k_a\Sigma_T + k_d - (k_a/k_{cat})r_P)r_R = -(k_aR + k_d)r_R \quad (33)$$

That is, the QSSA is not valid under the condition of excess of active sites.

- Under the QSSA, it is commonly considered that the reactant rate behavior is given by  $r_R \approx -r_P$ . In turn, this implies that the concentration of the intermediate complex is negligible. However, even if the first-order relaxation term  $\tau_R(R, P)\frac{dr_R}{dt}$  in Eq. (27) is discarded, the dynamics of the reactant concentration are described by

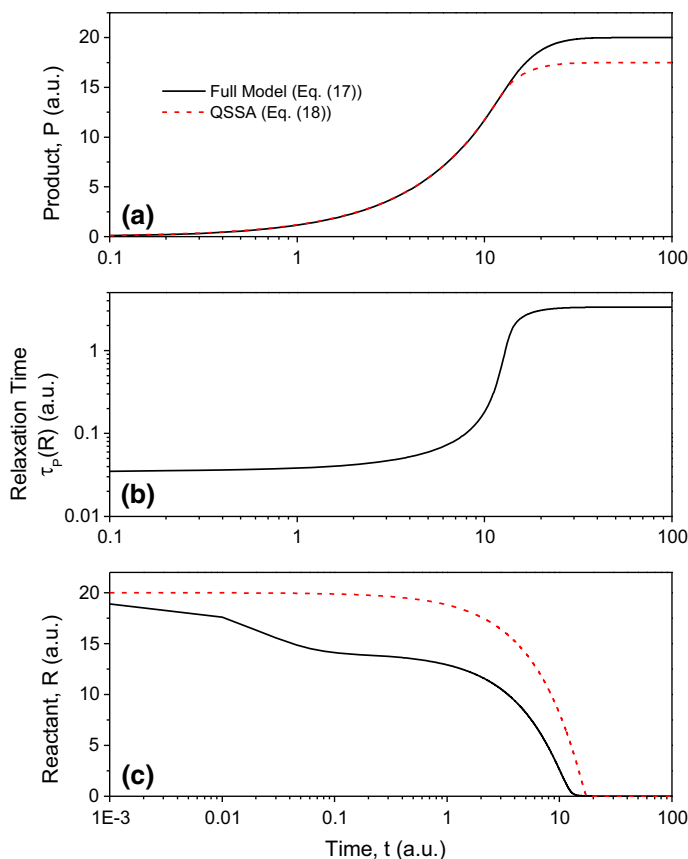
$$r_R \approx -\frac{(k_aR + k_d)r_P}{k_a\Sigma_T + k_aR + k_d - (k_a/k_{cat})r_P} \quad (34)$$

which can be approximated by  $r_R \approx -r_P$  only when the term  $k_aR + k_d$  is much larger than the term  $k_a\Sigma_T - (k_a/k_{cat})r_P$ . However, in such case one obtains the zero-order approximation given by Eq. (29). One concludes that in general the approximation  $r_R \approx -r_P$  cannot be justified. Overall, this result shows that the relation between the reactant and product rates is more involved than just taking the approximation  $r_R \approx -r_P$ .

The results commented above showed that in general the QSSA is not satisfied along typical batch reaction assays.

### 3.4 Numerical example

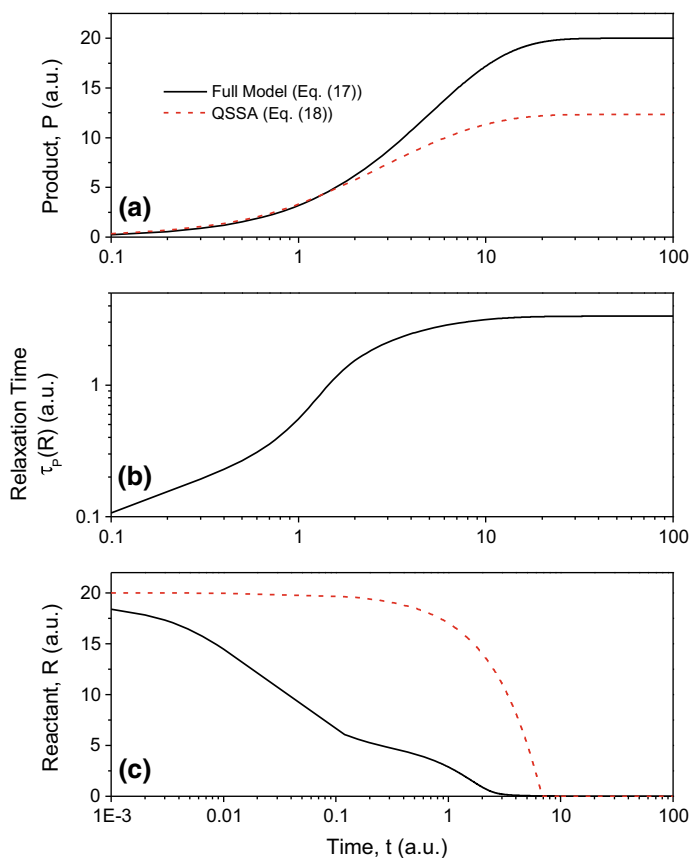
The analysis described above showed that the use of the QSSA can be justified when  $R \gg K_{LH}$ . However, even if the initial reactant load  $R_0$  is sufficiently large to satisfy



**Fig. 1** **a** Product concentration, **b** relaxation time, and **c** reactant concentration variations for a simulated case with  $k_a = 2$ ,  $k_d = 0.1$ ,  $k_{cat} = 0.2$ ,  $\Sigma_T = 6.0$  and  $R_0 = 20.0$ . All parameters and variables are expressed in arbitrary units (a.u.)

the inequality  $\tau_P(R) \ll 1$ , the reactant concentration  $R(t)$  decays along the reaction time in typical batch assays. Eventually, the constraint  $\tau_P(R) \ll 1$  cannot be fulfilled and the QSSA cannot be longer justified. Let us illustrate the above result with some numerical simulations. To this end, consider the following values expressed in terms of arbitrary units (a.u.):  $k_a = 2$ ,  $k_d = 0.1$ ,  $k_{cat} = 0.2$  and  $R_0 = 20.0$ . For this set of parameters one has that  $K_{LH} = 0.15$ , so that the initial condition  $R_0 = 20.0$  is in excess with respect to the LH constant. In this case, it is expected that the LH equation derived from the QSSA is satisfied for short reaction times. For  $\Sigma_T = 6.0$ , Fig. 1a compares the behavior of the product concentration obtained with the complete LH model Eq. (17) and the standard LH model given by Eq. (5). Good agreement between the product concentrations is found for times  $t \leq 13.0$ . However, for longer reaction times the standard LH equation leads to very poor estimates of the reactant concentration. This behavior can be explained by the lack of fulfillment of the constraint  $\tau_P(R) \ll 1$ . In fact, Fig. 1b presents the evolution of the relaxation time  $\tau_P(R)$ , showing that for short times the inequality  $\tau_P(R) \ll 1$  is satisfied. However, as

the reactant concentration decays for longer times, the constraint  $\tau_P(R) \ll 1$  cannot be satisfied. Besides, the standard LH equation underestimates the asymptotic value of the product concentration. As the relaxation time shows a step-like increase at about  $t = 13.0$ , the second-order effects  $\tau_P(R) \frac{d^2 P}{dt^2}$  in the differential form of the LH equation (27) cannot be discarded. Regarding the reactant concentration, Fig. 1a presents the results for the behavior obtained with the full model (Eq. 17) and the QSSA given by  $r_R \approx -r_P$ . The QSSA exhibits a very poor prediction since its derivation assumed that the dynamics of the adsorption complex concentration can be neglected. In the QSSA framework, one has that  $d\theta/dt \approx 0$  since the transformation  $R \rightarrow P$  is taking place at very short time scales. However, the results in Fig. 1c shows that the fast initial decrease of the reactant concentration was caused by the formation of a significant amount of adsorption complex, which led to important reduction of the reactant concentration. The performance of the LH equation derived from the QSSA becomes worse as the total concentration of active sites  $\Sigma_T$  is increased. An increase of the concentration of active sites will lead to a faster reduction of the



**Fig. 2** **a** Product concentration, **b** relaxation time, and **c** reactant concentration variations for a simulated case with  $k_a = 2$ ,  $k_d = 0.1$ ,  $k_{cat} = 0.2$ ,  $\Sigma_T = 15.0$  and  $R_0 = 20.0$ . All parameters are expressed in arbitrary units (a.u.)

reactant concentration, and hence to a faster violation of the constraint  $\tau_P(R) \ll 1$ . For  $\Sigma_T = 15.0$ , Fig. 2a shows that the estimation error in the product concentration is higher and appears at earlier times than for the smaller initial condition. Similarly, the poor performance of the standard LH equation is explained by the relatively high values of the relaxation time  $\tau_P(R)$ . Also, the QSSA for the reactant concentration is even worse since a higher amount of active sites converts a higher amount of initial reactant into adsorption complex.

## 4 Observability

In the above discussion, the system of differential equations related to the LH scheme was reduced to a second-order differential equation. In turn, the reaction rates for reactant and product concentrations meet a nonlinear relaxation process. However, the underlying relaxation processes of the reaction rates (see Eqs. 20, 24) involved a differential structure that is not affordable for most chemical kinetics and reactors practitioners. The system of differential equations given by (17) has still a clear physical interpretation, in terms of both parameters and concentration of chemical species. The problem with the system of differential equations (17) is that, in typical experimental assays, only the reactant concentration is available for measurements. An alternative to deal with this issue is to address the problem of whether the trajectory of the surface coverage fraction  $\theta(t)$  can be reconstructed from measurements of the reactant concentration trajectory  $R(t)$ . This problem is related to the observability properties of nonlinear systems, an issue that was elegantly addressed by Hermann and Krener [8]. Briefly, consider an autonomous dynamical system of the form

$$\begin{aligned}\frac{d\mathbf{x}}{dt} &= \mathbf{f}(\mathbf{x}) \\ \mathbf{y} &= \mathbf{h}(\mathbf{x})\end{aligned}\quad (35)$$

where  $\mathbf{x}$  is an  $n$ -dimensional vector of internal states and  $\mathbf{y}$  is an  $m$ -dimensional vector of measured outputs. It is said that the nonlinear system is observable if its  $n$ -dimensional state vector  $\mathbf{x}$  can be expressed univocally in terms of the  $m$ -dimensional measurements vector  $\mathbf{y}$  and its derivatives  $\{\mathbf{y}, d\mathbf{y}/dt, d^2\mathbf{y}/dt^2, \dots\}$  [8,9]. For the LH scheme, the observability problem is based on the reactant concentration and the covered surface fraction dynamics:

$$\begin{aligned}\frac{dR}{dt} &= \Sigma_T [-k_a (1 - \theta) R + k_d \theta] \\ \frac{d\theta}{dt} &= k_a (1 - \theta) R - (k_d + k_{cat})\theta\end{aligned}\quad (36)$$

In this way, one has that the state vector is  $\mathbf{x} = \{R, \theta\}$ , and the measured output is  $\mathbf{y} = R$ . The following expressions can thus be derived:

$$\begin{aligned}R &= \mathbf{y} \\ \theta &= \frac{\frac{d\mathbf{y}}{dt} + k_a \mathbf{y}}{k_a \mathbf{y} + k_d}\end{aligned}\quad (37)$$

Notice that Eq. (37) is nonsingular as long as  $k_a y + k_d = k_a R + k_d \neq 0$ , which is satisfied for mild physical conditions since the constants  $k_a$  and  $k_d$ , and the reactant concentration  $R$  are positive. This means that, given the system parameters, the dynamics of the complex concentration can be reconstructed from the dynamics of the measured reactant concentration. The main obstacle to achieve such dynamical reconstruction is to provide an accurate time-derivation of the measured output (i.e.,  $dR/dt$ ). In the presence of noise sampling in measurements, the derivative operator can exhibit poor performance. The general approach to address this issue is to use an observer to reconstruct asymptotically the internal states of the nonlinear system. In this regard, the following observer with input injection is proposed:

$$\begin{aligned}\frac{dR_{est}}{dt} &= \Sigma_T [-k_a(1 - \theta_{est})R_m + k_d\theta_{est}] + g_1(R_m - R_{est}) \\ \frac{d\theta_{est}}{dt} &= k_a(1 - \theta_{est})R_m - (k_d + k_{cat})\theta_{est} + g_2(R_m - R_{est})\end{aligned}\quad (38)$$

where  $\theta_{est}$  and  $R_{est}$  are estimates of  $\theta$  and  $R$ , respectively, and  $R_m$  is the measured reactant. On the other hand,  $g_1$  and  $g_2$  are tuning parameters. In the event that  $R_{est}(t) \rightarrow R_m(t)$ , the dynamics of Eq. (38) converges to the dynamics of the physical system modeled by Eq. (36). To establish the convergence properties, introduce the following parameterization of the observer gains:  $g_1 = \varepsilon^{-1}a_1$  and  $g_2 = \varepsilon^{-2}a_2$ , where  $\varepsilon$  is a positive parameter to be defined later, and  $a_1$  and  $a_2$  are some positive constants. Introduce the scaled error signals  $e_1 = \varepsilon^{-1}(R - R_{est})$  and  $e_2 = \theta - \theta_{est}$ , where  $\theta$  and  $R$  are the exact surface coverage fraction and reactant concentrations, respectively. Then, according to Eq. (36), it is convenient to re-write the dynamics of the scaled errors as follows:

$$\begin{aligned}\varepsilon \frac{de_1}{dt} &= \Sigma_T(k_a R_m + k_d)e_2 - a_1 e_1 \\ \varepsilon \frac{de_2}{dt} &= -\varepsilon(k_a R_m + k_d + k_{cat})e_2 - a_2 e_1\end{aligned}\quad (39)$$

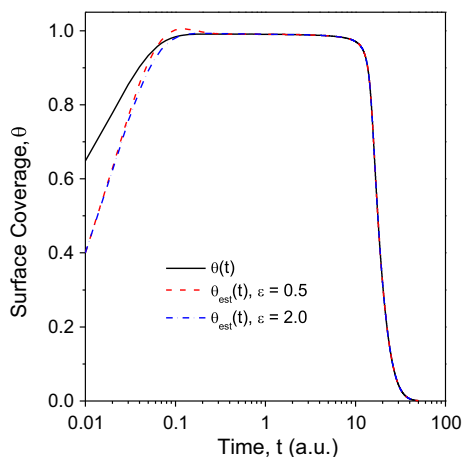
This is a singularly perturbed system with small parameter  $\varepsilon > 0$ . The reduced system is obtained by setting  $\varepsilon = 0$  in Eq. (39) to obtain the invariant manifold given by  $e_1 = 0$  and  $e_2 = 0$ . On the other hand, the boundary-layer system is obtained for the time scale  $t' = t/\varepsilon$ , so that the slow error dynamics is given by

$$\begin{aligned}\frac{de_1}{dt'} &= \Sigma_T(k_a R_m + k_d)e_2 - a_1 e_1 \\ \frac{de_2}{dt'} &= -a_2 e_1\end{aligned}\quad (40)$$

This system is equivalent to the following second-order differential equation:

$$\frac{d^2 e_2}{dt'^2} + a_1 \frac{de_2}{dt'} + a_2 \Sigma_T(k_a R_m(t) + k_d)e_2 = 0\quad (41)$$

**Fig. 3** Evolution of the estimated complex concentration for a simulated case with  $k_a = 2$ ,  $k_d = 0.1$ ,  $k_{cat} = 0.2$ ,  $\Sigma_T = 6.0$ ,  $R_0 = 20.0$  and  $\theta_0 = 0.4$ . All parameters are expressed in arbitrary units (a.u.)



Physically, the reactant concentration is uniformly bounded in the sense that  $R_m(t) \leq b$ , for given positive constant  $b$ . Also, for  $k_d > 0$  the time-varying coefficient satisfies  $\Sigma_T a_2 (k_a R_m(t) + k_d) > 0$  for all  $t > 0$ . In this way, Theorem 1.8 in Duc et al. [10] guarantees that the estimation error converges asymptotically to zero. In turn, this implies the asymptotic convergence  $\theta_{est}(t) \rightarrow \theta(t)$ . In other words, system (38) is able to provide an asymptotic estimate of the complex concentration based solely on measurements of the reactant concentration [11], solving the original observability problem.

#### 4.1 Numerical example

Let us illustrate the performance of the observer given by Eq. (38). Consider the following set of values with arbitrary concentration and time units:  $k_a = 2$ ,  $k_d = 0.1$ ,  $k_{cat} = 0.2$  and  $\Sigma_T = 6.0$ . The initial conditions are  $R_0 = 20.0$  and  $\theta_0 = 0.0$ . Set  $a_1 = 2.0$  and  $a_2 = 1.0$ . Assume the initial conditions  $R_{est,0} = 20.0$  and  $\theta_{est,0} = 1.0$ . Note that  $\theta_{est,0} \neq \theta_0$ , so the task of the observer (38) is to adjust the error in the initial condition of the adsorption complex. Figure 3 displays the evolution of the surface coverage fraction  $\theta$  and the corresponding estimate  $\theta_{est}$  for two different values of the observer parameter  $\varepsilon$ . The reaction time is extended for about 50 time units, while the convergence  $\theta_{est}(t) \rightarrow \theta(t)$  is achieved within the first 0.15 time units. This numerical result corroborates the proposal that observer (38) is a suitable estimator of the behavior of the concentration of the adsorption complex.

### 5 Estimation of the kinetic parameters

The estimation of the kinetic parameters of the LH scheme is an important experimental problem. For a given reactant depletion curve  $R(t)$  obtained from typical batch assays, one can pose a least-squares problem to estimate the kinetic parameters. The standard LH equation  $\frac{dR}{dt} = -\frac{\Sigma_T k_{cat} R}{K_{LH} + R}$  can provide only three independent parameters  $\{k_{cat}, \Sigma_T, K_{LH}\}$ , which are combinations of the original kinetic param-

ters  $\{k_a, k_d, k_{cat}, \Sigma_T\}$ . In contrast, the full model (i.e., when the quasi-steady state approximation is not assumed) given by Eq. (17) is able to provide the whole set of parameters. That is, Eq. (17) can be expressed as

$$\begin{aligned}\frac{dR}{dt} &= \Sigma_T [-k_a R + k_a \theta R + k_d \theta] \\ \frac{d\theta}{dt} &= k_a R - k_a \theta R - (k_d + k_{cat})\theta\end{aligned}\quad (42)$$

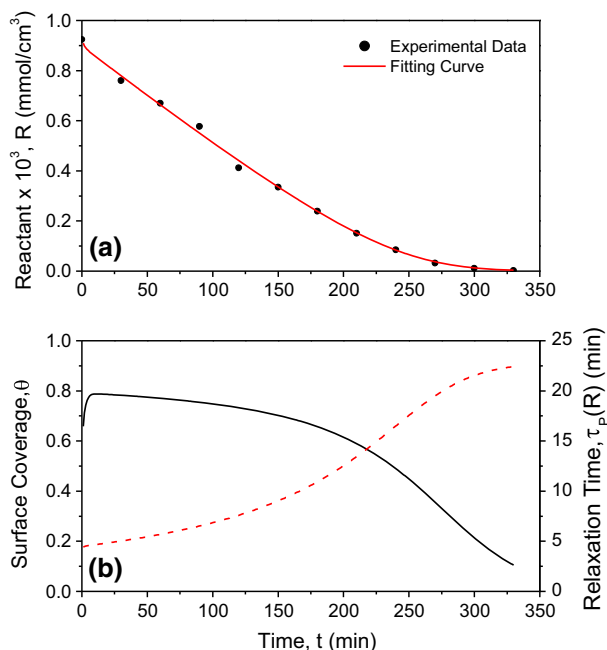
Independent parameters for Eq. (42) are combinations of the physical parameters; namely,  $b_1 \equiv \Sigma_T k_a$ ,  $b_2 \equiv \Sigma_T k_d$ ,  $b_3 \equiv k_a$  and  $b_4 \equiv k_d + k_{cat}$ . It can be seen that the estimation of these parameters leads univocally to the physical parameters as follows:  $k_a = b_3$ ,  $\Sigma_T = b_1/b_3$ ,  $k_d = b_2 b_3/b_1$  and  $k_{cat} = (b_4 b_1 - b_2 b_3)/b_1$ . Besides the fact that the standard LH equation is not in general an accurate description of the kinetics, the use of the exact model (42) is advantageous to estimate the full set of kinetic parameters from a single reactant depletion curve,  $R(t)$ . On the other hand, for a given measured depletion curve, say  $R_m(t)$ , the observability properties of the LH model guarantee the existence of a unique estimated trajectory for the adsorption complex  $\theta_{est}(t)$ . In fact, the observability of the system (42) from measurements of the reactant dynamics guarantees that the adsorption complex trajectory is uniquely determined (i.e., it does not introduce an additional degree-of-freedom) provided the initial condition is known in advance. In this connection, the adsorption complex trajectory  $\theta(t)$  acts merely as an internal state that does not affect the estimation of the kinetic parameters. Based on these features, the estimation of the kinetic parameters  $\{k_a, k_d, k_{cat}, \Sigma_T\}$  can be posed as a standard least-squares problem. If  $\{R_{m,1}, R_{m,2}, \dots, R_{m,N_d}\}$  are  $N_d$  experimental measurements of a depletion curve and  $\{R_{est,1}, R_{est,2}, \dots, R_{est,N_d}\}$  are the corresponding estimations based on Eq. (42), the objective function can be written as

$$J = \frac{1}{N_d} \sum_{i=1}^{N_d} (R_{m,j} - R_{est,j})^2 \quad (43)$$

The problem is the minimization of  $J$  to obtain estimates of  $\{k_a, k_d, k_{cat}, \Sigma_T\}$ . Non-negativeness of the kinetic parameters is imposed for the least-squares problem.

## 5.1 Example

To illustrate the estimation of the kinetic parameters, the photocatalytic degradation of phenol in aqueous solution was considered [12]. The photocatalytic reaction takes place under the action of  $\text{TiO}_2$  particles. The experimental assay started with an initial 60 min stage under darkness conditions to approach the equilibrium adsorption of phenol over the surface of the suspended  $\text{TiO}_2$  particles. Afterwards, the UV device was switched on to carry out the photocatalytic degradation of phenol. The initial phenol concentration before adsorption was  $1 \times 10^{-3} \text{ mmol cm}^{-3}$ . Figure 4a exhibits the experimental depletion data extracted from the work of Matos et al. [12]. It is noted that the initial phenol concentration is below  $1 \times 10^{-3} \text{ mmol cm}^{-3}$  because some phenol was adsorbed on the  $\text{TiO}_2$  surface in the preliminary adsorption stage.

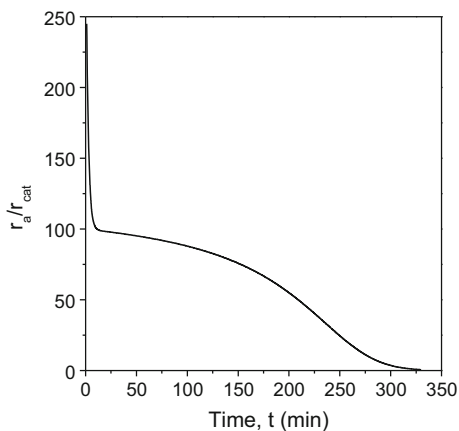


**Fig. 4** **a** Reactant depletion data for phenol photocatalytic degradation with TiO<sub>2</sub> particles [12]. The least-squares fitting made with the full model Eq. (4) is also shown. **b** Evolution of the adsorption complex (left axis) and the relaxation time (right axis) along the reaction time

The minimization of the objective function (43) was carried out by means of a random search algorithm, while the estimated data  $\{R_{est,1}, R_{est,2}, \dots, R_{est,N_d}\}$  was obtained by integration (fourth-order Runge–Kutta method with  $\Delta t = 10^{-2}$ ) of the two differential equations (43). Figure 4a also presents the adjusted curve, showing good agreement with experimental data. Figure 4b exhibits the corresponding evolution of the covered surface fraction  $\theta(t)$  (left axis), and the relaxation time  $\tau_p(R)$  (right axis). The adsorption complex shows a slight increase in the first four minutes to further decay gradually. It is noted that despite the measured reactant is practically zero, the surface coverage fraction shows a departure from zero (about 0.23). On the other hand, the relaxation time varies from 4.0 to 22 min, indicating that the QSSA leading to the standard LH equation is hardly satisfied. The estimated kinetic parameters for phenol photodegradation by TiO<sub>2</sub> particles are  $k_a = 8.9 \text{ cm}^3 \text{ mmol}^{-1} \text{ s}^{-1}$ ,  $k_d = 3.51 \times 10^{-5} \text{ s}^{-1}$ ,  $k_{cat} = 1.09 \times 10^{-5} \text{ s}^{-1}$  and  $\Sigma_T = 1.13 \times 10^{-4} \text{ mmol cm}^{-3}$ . The value of the LH (i.e., affinity) constant is  $K_{LH} = 7.96 \times 10^{-5} \text{ mmol cm}^{-3}$ . Let  $r_a = \Sigma_T k_a (1 - \theta) R$  and  $r_{cat} = \Sigma_T k_{cat} \theta$  be the adsorption and reaction rates. Figure 5 presents the variations of the ratio  $r_a/r_{cat}$  with the reaction time. It is noted that  $r_a/r_{cat} \gg 1$ , indicating that the adsorption step is faster than the reaction step. In turn, this implies that reaction is the controlling step in the phenol degradation by TiO<sub>2</sub> particles. For large reaction times, as the reactant concentration decreases by a larger amount, the adsorption step starts to be the controlling step.



**Fig. 5** Adsorption-to-reaction ratio  $r_a/r_{cat}$  as function of the reaction time. It is noted that  $r_a/r_{cat} \gg 1$ , indicating that the adsorption step is faster than the reaction step



## 6 Conclusions

This work considered the Langmuir–Hinshelwood (LH) scheme for a single reactant. By reducing the underlying system of differential equations to a single nonlinear relaxation process, it was shown that the commonly used QSSA rarely reflects the reaction dynamics for most practical conditions. In particular, it was shown that the QSSA is valid under high reactant concentration when the overall scheme behaves as a zero-order reaction. To avoid mistakes in the use of the LH scheme, it was concluded that the full set of LH equations should be used to describe the reactions dynamics. A problem with such approach is that adsorption complex concentrations are almost never measured. In this connection, it was proven that the dynamics of the adsorption complex concentration can be reconstructed from the reactant concentration trajectory. This observability property guaranteed the existence of a unique adsorption complex trajectory for a given measured reactant depletion curve. In turn, this allowed the use of the full LH model to estimate the set of kinetic parameters via the solution of a standard least-squares problem. Overall, the results in this work showed that the naïve approximation of the LH scheme via quasi-steady state assumptions can lead to important fitting and interpretation errors. As regarding this, given its observability properties, it can be concluded that the use of the detailed LH model should prevail over approximated inexact LH equations.

### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

## References

1. C.G. Hill, T.W. Root, *Introduction to Chemical Engineering Kinetics and Reactor Design* (Wiley, Hoboken, 2014)
2. M. Boudart, *Kinetics of Chemical Processes: Butterworth–Heinemann Series in Chemical Engineering* (Elsevier, Amsterdam, 2014)
3. K.V. Kumar, K. Porkodi, F. Rocha, *Catal. Commun.* **9**, 82 (2008)

4. D.Y. Murzin, Catal. Commun. **9**, 1815 (2008)
5. K.V. Kumar, K. Porkodi, A. Selvaganapathi, Dyes Pigments **75**, 246 (2007)
6. N.G. Asenjo, R. Santamaría, C. Blanco, M. Granda, P. Álvarez, R. Menéndez, Carbon **55**, 62 (2013)
7. D.T. Gillespie, J. Comput. Phys. **22**(4), 403 (1976)
8. R. Hermann, A. Krener, IEEE Trans. Autom. Control **22**, 728 (1977)
9. A. Isidori, *Nonlinear Control Systems* (Springer, New York, 1995)
10. L.H. Duc, A. Ilchmann, S. Siegmund, P. Taraba, Q. Appl. Math. **61**, 137 (2006)
11. H.K. Khalil, J.W. Grizzle, *Nonlinear Syst.* (Prentice Hall, New York, 1996)
12. J. Matos, J. Laine, J.M. Herrmann, Appl. Catal. B Environ. **18**, 281 (1998)