

Factors affecting the efficiency of a photocatalyzed process in aqueous metal-oxide dispersions Prospect of distinguishing between two kinetic models

Alexei V. Emeline^{a,b}, Vladimir Ryabchuk^b, Nick Serpone^{a,*}

^a Department of Chemistry and Biochemistry, Concordia University, 1455 deMaisonneuve Blvd. West, Montreal, Que., Canada H3G 1M8

^b Department of Photonics, Institute of Physics, University of Saint Petersburg, Saint Petersburg, Russia

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Abstract

The photooxidative degradation of phenol in aqueous TiO₂ dispersions has been revisited to determine the dependencies of the rate on the concentration of phenol and on the photon flow (ρ) of the actinic light at 365 nm. The principal objective was to assess the factors that influence the efficiency of the photocatalytic process, the rate of which is described by the function

$$\frac{dC}{dt}(\rho, C) = (\text{const})C^n \rho^m$$

where n and m are orders of the reaction with respect to concentration and photon flow (light intensity), respectively. The reaction order m varies with reagent concentration C , whereas the order n depends on photon flow ρ . The description indicates that $m \rightarrow 1$ if $n \rightarrow 0$, whereas $n \rightarrow 1$ if $m \rightarrow 0$. Therefore, the reaction orders m and n of phenol photodegradation are interdependent. A detailed kinetic description of the process is given based on two well-known mechanistic/kinetic models, namely (i) the Langmuir–Hinshelwood (LH) model whereby the organic reagent is pre-adsorbed on the photocatalyst surface prior to UV illumination, and (ii) the Eley–Rideal (ER) model for which the organic reagent diffuses from the solution bulk onto the photocatalyst surface to interact with the activated state of the photocatalyst. The kinetic treatment infers that it is possible (under certain conditions) to delineate between the LH and ER mechanistic models on the basis of the magnitude of the Langmuir constant K_L at very high photon flow, i.e. when $\rho \rightarrow \infty$ {for the LH pathway, $K_L \rightarrow K$; for the ER model $K_L \rightarrow 0$ }, and on the dependence of k_{obs} of the process on ρ . For the ER model, k_{obs} scales linearly with ρ at high photon flow, whereas for the LH pathway k_{obs} displays a sub-linear dependence on ρ and tends toward saturation at high photon flow. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Photodestruction of organic pollutants (e.g., phenols) in aqueous media has become one of the most important application of heterogeneous photocatalysis in the last decade [1–6]. Developing an effective technology for the photocatalytic purification of water requires knowledge of optimal process conditions. This goal can be achieved in either of two ways: (i) on the basis of statistics from a wide collection of experimental data, or (ii) from a clear understanding of the mechanism of a given photoprocess. Both require exten-

sive studies of the kinetics that include the dependencies of the rate of photodegradation on different experimental conditions (e.g., on the concentrations of the photocatalyst and reagents), on light intensity (i.e. photon flow), and on reactor geometry, among others. It is of no surprise that several research studies have dealt with the determination of such dependencies. The most valuable and systematic data most often reported concern the rate dependencies on the concentration of the organic pollutants [1,2,4,5,7–15].

Most dependencies of the photocatalytic reaction rates on the concentration of organic reagents have been described well by the Langmuir–Hinshelwood kinetic model (Eq. (1)).

$$\frac{dC}{dt} = \frac{k_{\text{obs}}K_L C}{(K_L C + 1)} \quad (1)$$

* Corresponding author. Fax: +1-514-848-2868.
E-mail address: serpone@vax2.concordia.ca (N. Serpone)

where k_{obs} is an apparent reaction rate constant, and K_L is the Langmuir constant reflecting the adsorption/desorption equilibrium between the reagent and the surface of the photocatalyst.

In more realistic and complex models employed to describe experimental dependencies of the rate on the concentration of reagents, we also need to consider the possible competition between the different reagents and/or solvent in the adsorption/desorption process. In this instance, the Langmuir–Hinshelwood kinetic model is characterized by Eq. (2) [11,16,17]:

$$\frac{dC}{dt} = \frac{k_{\text{obs}}K_L C}{(K_L C + \sum K_i C_i + 1)} \quad (2)$$

where K_i represents the adsorption/desorption constant of other reagents, or the kinetically significant intermediates, or the solvent with the corresponding concentrations C_i . Thus, according to Eqs. (1) and (2) the highest efficiency of the photocatalytic degradation of organic pollutants will be observed at relatively high concentrations of reagents to satisfy the conditions $K_L C \gg 1$ for Eq. (1), or $K_L C \gg \sum K_i C_i + 1$ for Eq. (2). Process efficiency will decrease with concentration decay during photodegradation. Consequently, in the case where photoprocesses take place via a Langmuir–Hinshelwood pathway, the important requirement for the photocatalyst will be its high capacity for ‘dark’ adsorption of the reagent as determined by K_L so as to maintain the value $K_L C$ high even at low concentrations of reagents.

Surprisingly, some workers continue to assume that observation of kinetics of a photocatalytic reaction which accord with either Eqs. (1) or (2) is a sufficient condition to infer that the Langmuir–Hinshelwood mechanism is the actual operational pathway. It has been demonstrated [7,10] however, that other mechanisms, including different modifications of the Eley–Rideal mechanism, can result in the same kinetics of photodegradation as represented by Eq. (1) with apparent constants k_{obs} and K_L for which the physical sense can be different and depends on the particular mechanism applied. Consequently, the required conditions for higher efficiencies of the photocatalyst may be somewhat different from its simple adsorption ability. In fact, for the mechanisms suggested by Turchi and Ollis [7] the apparent constant K_L represents the different combinations of the Langmuir constant, carrier trapping constants, and surface reaction constants, all of which infer that the corresponding processes are also important in order to achieve a higher efficiency for the photocatalyst. The rate constant k_{obs} depends on light intensity: at low photon flow k_{obs} scales linearly with light intensity, whereas at higher light intensity it scales with the square root of the light intensity. These features of the dependencies of reaction rates on light intensity were treated as a consequence of the bimolecular inter-band recombination of electrons and holes on the photocatalyst.

The linear and the square root dependencies of the rates of photoprocesses on light intensity have been observed by

many research groups [16,18–22]. Note that in some cases, the experimental data could be approximated neither by first order nor by second order reaction kinetics with regard to light intensity [10,11,23]. At very high light intensities, Ollis [18] observed that the order of the reaction approached 0. This was explained in terms of a diffusion limitation on the transport of the reagent molecules to the photocatalyst surface. In spite of the increase of the reaction rate with light intensity until it reaches a plateau, the efficiency η and the quantum yield Φ of photodegradation are greatest in the linear regime of the dependence on light intensity, and then decrease with increase in light intensity, as inferred from Eq. (3).

$$\eta = \frac{((dC(\rho))/dt)}{\rho} \quad (3)$$

where

$$\frac{dC}{dt} \propto \rho; \quad \eta = (\text{const}) \quad (\text{low light intensity})$$

$$\frac{dC}{dt} \propto \rho^{1/2}; \quad \eta = (\text{const})\rho^{-1/2} \quad (\text{high light intensity})$$

$$\frac{dC}{dt} \propto \rho^0; \quad \eta = (\text{const})\rho^{-1} \quad (\text{very high light intensity})$$

The dependencies of the rates of photocatalytic processes on the concentration of reagents are basically and most often measured only at some given light intensity, whereas the rate dependencies on photon flow are typically obtained for only one particular concentration of the reagents. It is fairly common to observe that kinetic parameters obtained in different studies do not accord with each other, which suggests that they depend not only on the different experimental conditions used but on other factors as well. In particular, parameters of rate dependencies on concentration may vary with light intensity, and in turn parameters of rate dependencies on light intensity may depend on the concentration of reagents [10,19], and/or on the presence of carrier scavengers (e.g., O_2 and H_2O_2) [20]. Thus, to produce more effective photocatalysts for water purification one needs a better understanding of the interconnection between intrinsic properties of photocatalysts and the experimental conditions, that include the concentration of reagents and light intensity.

The major purpose of the present study was to determine the more favorable factors (conditions) for the photocatalytic destruction of organics (e.g., phenols) in aqueous solutions in the presence of the metal oxide TiO_2 , and to understand what conditions should be used to increase the efficiency of the photocatalytic processes.

2. Experimental

In our experiments on the dependence of the photooxidation of aqueous phenolic solutions on light intensity and

concentration of phenol, we used ‘Degussa’ P25 TiO₂ as the photocatalyst. Experiments were carried out at pH=3 (HCl). Phenol concentrations were measured by liquid chromatography with an HPLC chromatograph (‘Waters’ 501 pump and ‘Waters’ μ Bondapak C18 column) connected to a ‘Shimadzu’ flow cell for absorption recording with the ‘Shimadzu UV-265’ spectrophotometer that was interfaced to an IBM PC computer. Recording parameter settings, data collection, and data processing were carried out using the ‘Spectroscopy Interface Software, Version 3’ (Shimadzu Scientific Instruments, Inc.). Irradiation of a phenol solution with a TiO₂ loading of 0.3 g l⁻¹ was carried out with an Oriel 1000-W Hg/Xe lamp in a sphere-like pyrex reactor. An interference filter selected the 365 nm actinic light. Non-selective ‘gray’ metal supported pyrex filters were used to attenuate the photon flow.

3. Results

Rates of phenol photodegradation dC/dt versus initial phenol concentration C at various photon flow are plotted in Fig. 1. Initial rates dC/dt were determined by differentiation of $C(t)$ kinetic curves (dependence of concentration on exposure time, $C(t)$). The highest photon flow ($\rho_0 = (1.1 \pm 0.3) \times 10^{17}$ photons cm⁻² s⁻¹ at $\lambda = 365$ nm) is henceforth taken as the unit of measure of photon flow.

All curves of the set were approximated by Eq. (1) and values of the constants k_{obs} and K_L are presented in Table 1 and plotted in Fig. 2.

The results show that both constants in Eq. (1) depend on photon flow: k_{obs} depends linearly on photon flow, whereas the constant K_L decreases with an increase in photon flow. In such case, K_L cannot be considered a Langmuir con-

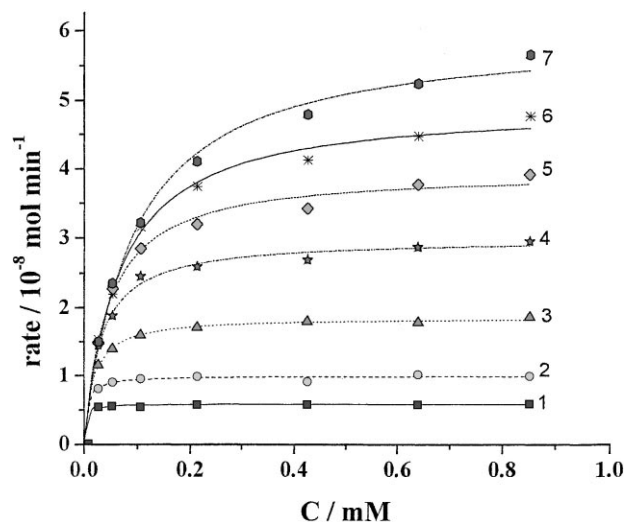


Fig. 1. Dependencies of the rate of phenol photodegradation on the phenol concentration C at different photon flow of the actinic light at 365 nm: (1) $\rho = 0.06\rho_0$, (2) $\rho = 0.12\rho_0$, (3) $\rho = 0.29\rho_0$, (4) $\rho = 0.5\rho_0$, (5) $\rho = 0.65\rho_0$, (6) $\rho = 0.86\rho_0$, (7) $\rho = \rho_0$.

Table 1
Experimental data of K_L and k_{obs} at different relative light intensities

ρ/ρ_0	k_{obs} (10^{-8} mol min ⁻¹)	K_L (10^5 M ⁻¹)
0.06	0.58	4.089
0.12	0.99	1.759
0.29	1.85	0.588
0.5	2.98	0.347
0.658	3.96	0.234
0.865	4.93	0.158
1	5.99	0.112

stant which reflects the adsorption/desorption equilibrium ($K_L = k_{\text{ads}}/k_{\text{des}}$) in Eq. (1).

The family of curves dC/dt versus ρ at various phenol concentrations C was also obtained in the subsequent set of experiments; they are portrayed in Fig. 3. It is clear that the rate of phenol photodegradation dC/dt approaches linearity with photon flow ρ only at high phenol concentrations (see curve 7 in Fig. 3).

Starting from the high intensity limit, the smaller the concentration of phenol the greater is the deviation of the $\{dC/dt\}(\rho)$ curve from linearity. At the lowest initial concentration of phenol, $C = 0.027$ mM (curve 1), the $\{dC/dt\}(\rho)$ dependence becomes extremely sub-linear. In fact, it is close to saturation at $\rho > 0.5\rho_0$. In general, all the dependencies on photon flow, ρ , can be approximated by the function:

$$r(\rho) = \frac{a b \rho}{(1 + b \rho)} \quad (4)$$

where a and b are constants at a given concentration of phenol C . The dependencies of these constants on phenol concentration are presented in Fig. 4. We note that the parameter a depends linearly on concentration C , whereas b decreases with increase in concentration via a hyperbolic decay function. Thus a scales with ρ and b scales with ρ^{-1} . The corresponding values of a and b are presented in Table 2.

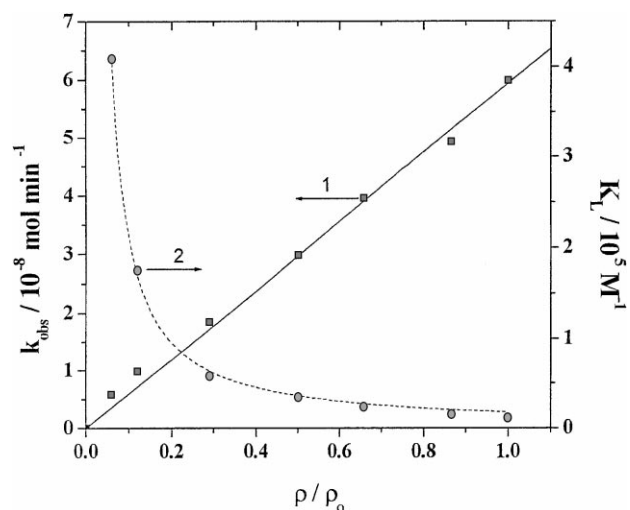


Fig. 2. Dependencies of the rate constant k_{obs} (1) and the Langmuir constant K_L (2) on photon flow of the actinic light at 365 nm.

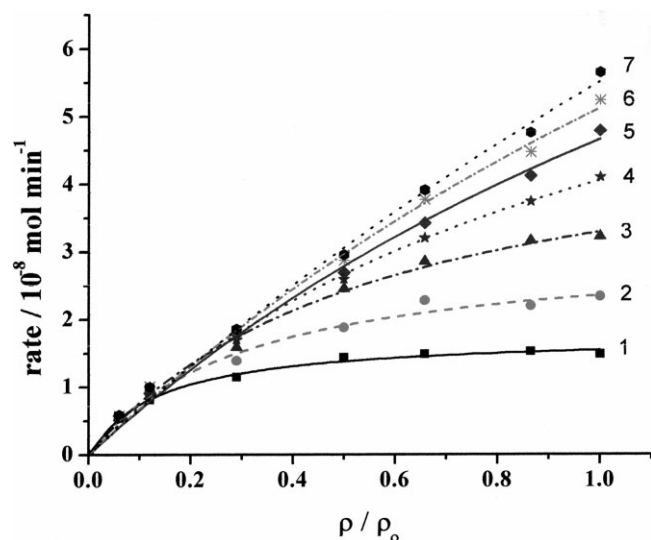


Fig. 3. Dependencies of the rates of phenol photodegradation on the relative photon flow ρ/ρ_0 of the actinic light at 365 nm and at different initial concentrations of phenol: (1) $C=0.027$ mM, (2) $C=0.053$ mM, (3) $C=0.106$ mM, (4) $C=0.213$ mM, (5) $C=0.427$ mM, (6) $C=0.638$ mM, (7) $C=0.851$ mM.

Eq. (4) is equivalent to Eq. (1) provided that $a(C)$ and $b(C)$ in Eq. (4) satisfy the above mentioned conditions, i.e. $a \propto C$ and $b \propto C^{-1}$; as well, Eq. (1) corresponds to Eq. (4) for $k_{\text{obs}} \propto \rho$ and $K_L \propto \rho^{-1}$ (see above). In other words, the functions that describe the experimental $\{dC/dt\}(\rho, C)$ dependencies of the rates of phenol photodegradation (Eqs. (1) and (4)) are equivalent. The $\{dC/dt\}(\rho, C)$ dependence on ρ and C can thus be generalized as:

$$\left(\frac{dC}{dt}\right)(\rho, C) = \frac{\alpha\rho C}{(\beta\rho + \gamma C)} \quad (5)$$

where the coefficients α , β , and γ are independent of light intensity and phenol concentration. The surface depicting

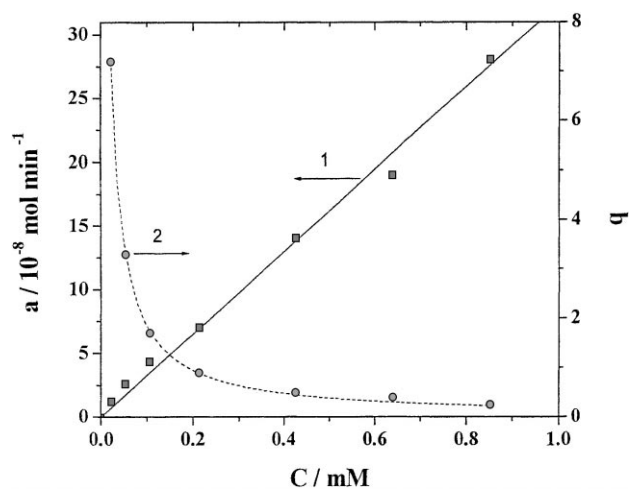


Fig. 4. Dependencies of the approximation parameters a (1) and b (2) on the initial concentration of phenol C .

Table 2

Experimental data of parameters a and b at different concentrations of phenol

C (mM)	a (10^{-8} mol min $^{-1}$)	b
0.0215	1.2	7.2
0.0533	2.6	3.3
0.1066	4.3	1.7
0.2126	7	0.9
0.4256	14	0.5
0.6384	19	0.4
0.8512	28	0.25

the experimental dependence of the rate of phenol photodegradation on both photon flow and phenol concentration is presented in Fig. 5. Note that Eq. (5) can be cast into the Langmuir–Hinshelwood form (Eq. (1)) when the photon flow ρ is constant.

The rate of the photocatalyzed reaction can also be described by the function:

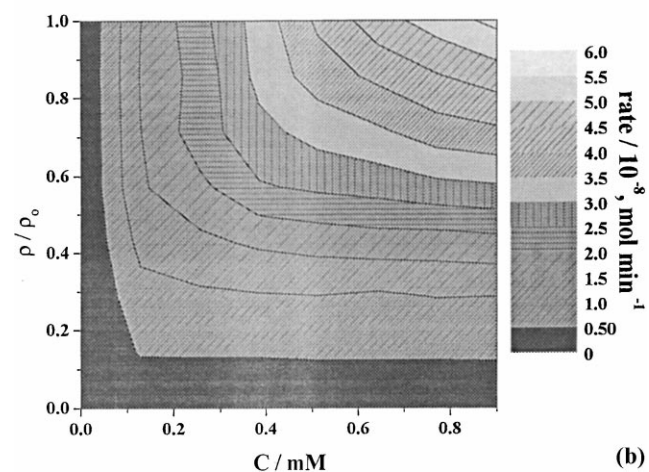
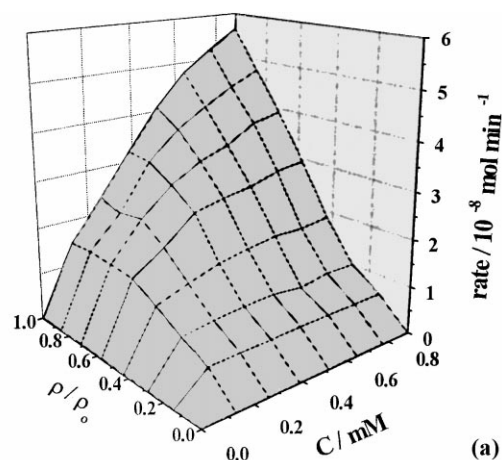


Fig. 5. (a) Three-dimensional dependence of the rate of phenol photodegradation on its concentration and on photon flow of the actinic light; (b) Map-like projection of the dependence of the rate of phenol photodegradation on its concentration and photon flow of the actinic light.

$$\frac{dC}{dt}(\rho, C) = (\text{const})C^n \rho^m \quad (6)$$

where n and m are orders of the reaction on concentration and light intensity, respectively. The reaction order m in Eq. (6) varies with reagent concentration in accordance with Eq. (5); m approaches unity as $C \rightarrow \infty$ (i.e. for $\gamma C \gg \beta \rho$) and conversely $m \rightarrow 0$ if $C \rightarrow 0$ (or if $\gamma C \ll \beta \rho$). Similarly, the order n approaches unity if $\rho \rightarrow \infty$ at $\beta \rho \gg \gamma C$ and conversely $n \rightarrow 0$ if $\rho \rightarrow 0$ (or if $\beta \rho \ll \gamma C$). In other words, $m \rightarrow 1$ if $n \rightarrow 0$, whereas $n \rightarrow 1$ if $m \rightarrow 0$. Therefore, the reaction orders m and n of phenol photodegradation are interdependent.

4. Discussion

For a titania/phenol aqueous heterogeneous system, photoexcitation of TiO_2 by light absorption occurs within the spectral range 300–400 nm, under the conditions used. A result of this primary photoexcitation of the photocatalyst is the generation of electron/hole pairs (Eq. (7)). Those photocarriers



capable of reaching the photocatalyst surface may participate in surface chemical processes. Thus, regardless of the mechanism of the photocatalytic process, its rate depends on the surface concentration of the corresponding charge carriers, n_s . The latter is determined by the rate of carrier flow (due to diffusion and/or drift) from the bulk to the surface, J_s , by the rate of photogeneration of carriers on the surface, G_s and by their decay through surface recombination and reaction pathways s (Eq. (8)):

$$\frac{\partial n_s}{\partial t} = J_s + G_s - sn_s = 0 \quad (8)$$

Hence

$$n_s = \frac{J_s + G_s}{s} \quad (9)$$

where $J_s = -D \partial n(\rho)/\partial \theta + \mu n(\rho)\mathcal{E}$ represents the sum of diffusion and drift flows, respectively; D is the diffusion coefficient of carriers, $\partial n(\rho)/\partial \theta$ is a spatial gradient of carrier concentration at the surface which depends on the photon flow of the actinic light, ρ ; μ is the mobility of the carriers, and \mathcal{E} is the electric field at near-surface space of the photocatalyst. Also, $G_s = \chi \phi \rho$, where χ is a surface absorption coefficient, ϕ is the quantum yield of carrier generation, and $s = R_s + kS$, where R_s is the rate of the ‘physical’ pathway of carrier recombination on the surface, and kS is an apparent bimolecular rate of carrier decay in the surface chemical process. Note that k is a real constant of the first step of the surface chemical process, and S is the concentration of the surface reactive sites that trap the carriers. These sites may be adsorbed molecules or surface carrier traps, that is (photo)catalytic centers [24].

It is relevant to point out that Eq. (8) cannot be used to calculate the exact surface concentration of carriers since it is only one of the set of equations needed to be solved. The whole set includes the continuity equation with boundary conditions represented by Eq. (8) and by time evolution (initial) conditions. The solution of the continuity equation depends on the given model used to describe the photocatalyst particle, and consequently may vary for different models applied. However, the boundary condition (Eq. (8)) for the surface concentration of carriers remains valid for any model, and thus can be employed to analyze the experimental dependencies of reaction rates on reagent concentration and photon flow.

The rate of the surface limiting primary step (Eq. (10)):



can be described by Eqs. (11a) and (11b)

$$\frac{dC}{dt} = k_9 [h_s^+] S \quad (11a)$$

$$\frac{dC}{dt} = \frac{(J_s + G_s)k_9 S}{(R_s + k_9 S)} \quad (11b)$$

Both J_s and G_s may be considered as linear functions of the photon flow ρ of the actinic light (Eq. (12)), that is,

$$(J_s + G_s) = (\text{const})\rho \quad (12)$$

provided that the concentration of carriers in the bulk is proportional to the light intensity, valid if the carrier lifetime is independent of the light intensity. This suggestion is realistic for real (but not ideal) solids since the main path of carrier decay in such solids at relatively moderate excitation is through carrier trapping by and recombination through solid defects [25,26], whose concentration is about $10^{16} - 10^{18} \text{ cm}^{-3}$, much greater than the concentration of free carriers at the given conditions.

Further considerations depend on what type of mechanism is invoked to interpret the experimental results obtained. Generally, two different mechanisms are considered to describe photocatalytic processes in heterogeneous systems: (a) the Langmuir–Hinshelwood (LH) mechanism where reagents are pre-adsorbed on the surface of the photocatalyst before photoactivation of the system, and (b) the Eley–Rideal (ER) pathway when reagents in solution react with the activated state of the photocatalyst surface. We examine the former in some detail since it is the one most often invoked by many researchers.

4.1. Langmuir–Hinshelwood mechanism

In invoking the frequently used LH mechanism, it is often assumed that establishment of the adsorption/desorption process does not limit the rate of the photocatalytic reaction. That is, the concentration of adsorbed molecules (S in Eqs. (11a) and (11b)) depends on the concentration of the reagent

in solution, C , through the Langmuir adsorption isotherm (Eq. (13)):

$$S = \frac{S_0 KC}{(KC + 1)} \quad (13)$$

Using the Langmuir constant ($K=3.14 \times 10^3 \text{ M}^{-1}$) and the maximal coverage ($S_0=1.4 \times 10^{-6} \text{ mol m}^{-2}$) for dark adsorption of phenol on TiO_2 (P25) reported by Matos et al. [15], we deduce that in our experiments even at the highest concentration of phenol, $C=8.51 \times 10^{-4} \text{ M}$, no complete saturation of the surface by adsorbed molecules occurs. That is, KC is not greater than unity, and the coverage S is $1.0 \times 10^{-6} \text{ mol m}^{-2}$. It is also worth noting that the Langmuir constant for dark adsorption is about two orders of magnitude smaller than the apparent constants K obtained in the present work for the photoprocess kinetic approximation at the lowest light intensity (see Table 1). The result of substituting S in Eq. (13) into Eq. (11b) yields a dependence corresponding to Eq. (1), namely

$$\frac{dC}{dt} = \frac{(\text{const})\rho k_{10} S_0 KC}{R_s((R_s + k_{10} S_0)(KC/R_s) + 1)} \quad (14)$$

provided that

$$k_{\text{obs}} = \frac{(\text{const})\rho k_{10} S_0}{R_s + k_{10} S_0} \quad (15)$$

and

$$K_L = \frac{(R_s + k_{10} S_0)K}{R_s} \quad (16)$$

Obviously, the simplest type of Langmuir–Hinshelwood kinetics will be obtained only if the influence of the surface chemical reaction rate, kS , on the total rate of surface recombination s is negligible, i.e. $R_s \gg kS$. In this case, the resulting expression will be,

$$\frac{dC}{dt} = \frac{(((\text{const})\rho k_{10})/R_s)S_0 KC}{KC + 1} \quad (17)$$

which is equivalent to Eq. (1) with

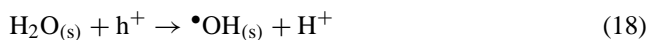
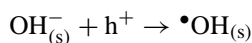
$$k_{\text{obs}} = \{(\text{const})\rho k_{10}/R_s\}S_0.$$

Thus, K_L does not depend on photon flow (Eq. (16)) and the only reason for observing the rate dependence on light intensity is a dependence of k_{obs} (i.e., J_s and G_s) on the intensity of the absorbed light (Eq. (15)). Clearly, this simple LH model represented by Eqs. (14) and (17) is inconsistent with the experimental dependencies observed in Fig. 2. The only possibility of observing the interdependence of the rate constants on the concentration of reagents and light intensity is if the surface chemical reaction affects the ‘physical’ process of surface recombination, which we examine next.

4.2. Recombination decay of active centers and intermediates in photocatalyzed reactions

There exists a widespread consensus that a major oxidizing role in surface photochemical reactions is played by the

surface OH^- groups and/or adsorbed water, which form the $\bullet\text{OH}$ radicals by trapping of surface holes [1–7].



Generation of $\bullet\text{OH}$ radicals occurs regardless of the presence or absence of organic reagents at some constant rate of a given photon flow. As well, generation of $\bullet\text{OH}$ radicals is a part of, if not a major path of the surface recombination of holes. Then, in terms of Eq. (10) the rate of generation of $\bullet\text{OH}$ radicals is given by,

$$r_{18} = k_{18}[h_s^+][\text{OH}_{(s)}^-] \quad (19a)$$

$$r_{18} = \frac{(\text{const})\rho k_{18}[\text{OH}_{(s)}^-]}{s} \quad (19b)$$

Such active species as $\bullet\text{OH}$ radicals readily attack organic molecules that are either pre-adsorbed on the surface (LH model) or are dissolved in water (ER model).



In each case, the rate of phenol photodegradation is given by,

$$\frac{dC}{dt} = k_{20}[\bullet\text{OH}_{(s)}][\text{PhOH}]$$

At the same time, these $\bullet\text{OH}$ active species do not accumulate on the surface in the absence of organic reagents, which means that their lifetime is rather short. Turchi and Ollis [7] suggested that the stage of physical deactivation of $\bullet\text{OH}$ radicals is thermal detrapping of holes, namely,



Consequently, the concentration of $\bullet\text{OH}$ radicals in a quasi steady-state approach will be given by,

$$[\bullet\text{OH}_{(s)}] = \frac{(\text{const})\rho k_{18}[\text{OH}_{(s)}^-]}{s(k_{20}[\text{PhOH}] + k_{21})} \quad (22)$$

and the rate of phenol photodegradation is given by

$$\frac{dC}{dt} = \frac{(\text{const})\rho k_{18}[\text{OH}_{(s)}^-]k_{20}[\text{PhOH}]}{s(k_{20}[\text{PhOH}] + k_{21})} \quad (23)$$

for $\bullet\text{OH}$ radical attack of the phenol molecules diffusing from the solution bulk to the photocatalyst surface (ER model), and is given by Eq. (24):

$$\frac{dC}{dt} = \frac{(\text{const})\rho k_{18}[\text{OH}_{(s)}^-]k_{20}K[\text{PhOH}_{(s)}]}{s((k_{20}S_0 + k_{21})K[\text{PhOH}_{(s)}] + k_{21})} \quad (24)$$

for pre-adsorbed phenol on the photocatalyst surface (LH model).

Eqs. (23) and (24) are similar to those obtained by Turchi and Ollis [7]. However, they do not provide an explanation of the interdependence of reaction rates on light intensity and on the concentration of reagents as observed in our experiments. The interdependence can be rationalized if recombination of $\bullet\text{OH}$ radicals with surface electrons, rather than thermal deactivation, is the major path of decay of $\bullet\text{OH}$ radicals.



which means either that in Eqs. (21)–(24)

$$k_{21} = k_{25}[e^-] \quad (26)$$

or taking into consideration that the concentration of electrons on the surface follows Eq. (9)

$$k_{21} = \frac{k_{25}(J_e + G_e)}{s_e} \quad (27a)$$

$$k_{21} = \frac{k'_{25}\rho}{s_e} \quad (27b)$$

We can then describe the rate of photodegradation of phenol via the ER mechanism (Eq. (28)), as

$$\frac{dC}{dt} = \frac{(\text{const})\rho k_{28}[\text{OH}_{(s)}^-]k_{20}[\text{PhOH}]}{s(k_{20}[\text{PhOH}] + ((k'_{25}\rho)/s_e))} \quad (28)$$

The rate of phenol photodegradation according to the LH model can be described by Eq. (29) as

$$\frac{dC}{dt} = \frac{(\text{const})\rho k_{18}[\text{OH}_{(s)}^-]k_{20}K[\text{PhOH}_{(s)}]}{s((k_{20}S_o + ((k'_{25}\rho)/s_e))K[\text{PhOH}] + ((k'_{25}\rho)/s_e))} \quad (29)$$

Note that Eq. (28) can easily be transformed either into Eq. (1) if

$$K_L = \frac{k_{20}}{((k'_{25}\rho)/s_e)} \quad \text{that is, } K_L \propto \rho^{-1} \quad (30)$$

and

$$k_{\text{obs}} = \frac{(\text{const})\rho k_{18}[\text{OH}_{(s)}^-]}{s} \quad \text{that is, } k_{\text{obs}} \propto \rho \quad (31)$$

or into Eq. (4) if in Eq. (28).

$$a = \frac{(\text{const})\rho k_{18}[\text{OH}_{(s)}^-]k_{20}[\text{PhOH}]}{s} \quad \text{that is, } a \propto C \quad (32)$$

$$b = \frac{(k'_{25}/s_e)}{k_{20}[\text{PhOH}]} \quad \text{that is, } b \propto C^{-1} \quad (33)$$

Consequently, Eq. (28) describes completely all the experimental dependencies obtained in the present work.

The LH kinetic expression 29 can also be cast into Eq. (1) provided that

$$K_L = \frac{(k_{20}S_o + ((k'_{25}\rho)/s_e))K}{((k'_{25}\rho)/s_e)} \quad \text{that is, } K_L \propto \rho^{-1} \quad (34)$$

and

$$k_{\text{obs}} = \frac{(\text{const})\rho k_{18}[\text{OH}_{(s)}^-]k_{20}S_o}{k_{20}S_o + ((k'_{25}\rho)/s_e)} \quad (35)$$

that is,

$$k_{\text{obs}} \propto \frac{k_{20}S_o\rho}{k_{20}S_o((k'_{25}\rho)/s_e)}$$

The latter dependence, as described by Eq. (35), does not correspond to our experimental results. However, if $k_{20}S_o \gg (k'_{25}\rho)/s_e$, that is if $\bullet\text{OH}$ radicals react with adsorbed molecules of phenol faster than they recombine with surface electrons, then from Eqs. (34) and (35)

$$K_L = \frac{k_{20}S_o K}{((k'_{25}\rho)/s_e)} \quad (36)$$

and

$$k_{\text{obs}} = (\text{const})\rho k_{18}[\text{OH}_{(s)}^-] \quad (37)$$

or $K_L \propto \rho^{-1}$ and $k_{\text{obs}} \propto \rho$, which satisfies the experimental data (Fig. 2). The particular reason for the slower recombination with surface electrons could be a slower rate of electron transport (see Eqs. (27a) and (27b)) from the bulk to the surface because of an accumulation of a negative charge on the photocatalyst surface.

Consequently, both LH and ER mechanisms involving attack of phenol by photogenerated $\bullet\text{OH}$ radicals on the particle surface and their decay by recombination with surface electrons can be used to interpret the experimental results presented in this work.

5. Concluding remarks

The fundamental result of the present study is the observation of the interdependence of the reaction rate of phenol photodegradation on photon flow and concentration of phenol. The characteristic of this interdependence permits to define the practical conditions to achieve the higher efficiency of the photocatalytic process. In particular, on altering the photon flow it is possible to maintain the rate dependence in the saturated regime with respect to concentration even at low values of ρ . Moreover, it automatically provides the linear regime of the rate dependence on photon flow, a condition for the highest efficiency of a photoprocess (see Section 1). In any case, to keep the efficiency or quantum yield high, lower concentrations require lower photon flow that leads to a lower rate of photodegradation. Consequently, to achieve a high efficiency for the photooxidative degradation of water pollutants we must look at the essential role of the properties of the photocatalyst.

On the basis of the proposed LH and ER mechanisms for the photodegradation of phenol, we conclude that in order to observe the interdependence of reaction rates on the

concentration of reagents and on light intensity, the essential role is played by the influence of surface chemical reactions on the surface recombination of carriers, particularly by shifting the decay of photogenerated $\bullet\text{OH}$ radicals from a 'physical' path of recombination with electrons to a chemical attack of organic molecules. However, analysis of both ER and LH kinetics (Eqs. (28) and (29)) shows that although the optimal conditions that apply to the (photo)catalysts and heterogeneous systems may be similar, *they are not exactly identical*. To observe a higher efficiency of photodegradation in the case of an operational ER mechanism, Eq. (38) must be valid.

$$\frac{dC}{dt} = \frac{(\text{const})\rho k_{18}[\text{OH}_{(s)}^-]}{s} \quad (38)$$

To obtain the maximal rate of photogeneration of $\bullet\text{OH}$ radicals, the condition expressed by Eq. (39) must be

$$k_{20}[\text{PhOH}] \gg \frac{k'_{25}\rho}{s_e} \quad (39)$$

satisfied (see Eq. (28)). In other words, the rate of the chemical reaction must be much faster than the rate of recombination of surface $\bullet\text{OH}$ radicals with surface electrons. The former might be achieved by increasing the concentration of phenol. However, the effective photocatalyst should be able to work with high efficiency even at low concentrations of phenol (see Section 1). Since k_{20} is a constant of interaction of surface $\bullet\text{OH}$ radicals with organic molecules, which is likely not affected by the photocatalyst, and since a decrease in light intensity decreases the total rate of photodegradation (Eq. (38)), the only possible way for photocatalyst modification is to decrease k'_{25}/s_e . That is (see e.g. Eq. (28)), we need (i) to decrease the electron flow from the bulk to the surface, caused by a shorter diffusion length or by a near-surface electric field, and (ii) to modify the surface active sites (i.e., decrease the number of surface OH^- groups) so as to decrease the cross-section of electron trapping. Another well-known possibility of increasing the efficiency of the photocatalytic process is addition of electron scavengers (e.g., O_2 and H_2O_2) into the system which will increase the surface loss of electrons, s_e . Note that the condition in Eq. (39) for maximal efficiency of the photocatalyst corresponds to saturation of the rate dependence on the concentration of phenol and its linear dependence on photon flow, as noted earlier in the Introduction.

For the LH mechanism (Eq. (29)), saturation of the rate dependence on reagent concentration is achieved when

$$(k_{20}S_0 + ((k'_{25}\rho)/s_e))K[\text{PhOH}_{(s)}] \gg \frac{k'_{25}\rho}{s_e} \quad (40)$$

All our considerations regarding the ER mechanism remain valid. However, as is typical for the LH mechanism, the Langmuir constant K for the adsorption/desorption equilibrium plays an important role in efforts to increase the photocatalytic efficiency. The condition expressed by Eq. (40) is

an essential but not a sufficient condition to achieve the highest efficiency from a photocatalyst, since the dependence on light intensity becomes highly sub-linear:

$$\frac{dC}{dt} = \frac{(\text{const})\rho k_{18}[\text{OH}_{(s)}^-]k_{20}S_0}{s(k_{20}S_0 + ((k'_{25}\rho)/s_e))} \quad (41)$$

Consequently, an additional condition must be applied, namely that

$$k_{20}S_0 \gg \frac{k'_{25}\rho}{s_e} \quad (42)$$

in order to observe the linear dependence of the reaction rate on light intensity. Thus,

$$\frac{dC}{dt} = \frac{(\text{const})\rho k_{18}[\text{OH}_{(s)}^-]}{s} \quad (43)$$

which corresponds exactly to the maximal rate of the photocatalytic process for the ER mechanism (see Eq. (38)).

In spite of the similar behavior of ER and LH kinetics, there is nevertheless a subtle difference in the approximations of the apparent constants k_{obs} and K_L (Eq. (1)) in the different mechanistic models. For example, at very high photon flow (i.e., when $\rho \rightarrow \infty$) $K_L \rightarrow 0$ in the ER pathway, whereas $K_L \rightarrow K$ in the LH mechanism. Unfortunately, the low value of the Langmuir constant for *dark* adsorption of phenol on TiO_2 particles ($K \sim 3.14 \times 10^3 \text{ M}^{-1}$) [15] compared to the apparent experimental values of K_L ($\sim 10^4$ – 10^5 M^{-1}) cannot be distinguished from 0 within experimental error. However, it is possible (in principle) to use different heterogeneous systems which will display higher *dark* adsorption constants such that the two kinetic models may be distinguished. Another difference between the ER and LH mechanisms lies in the dependence of k_{obs} on light intensity. For the ER model k_{obs} scales linearly with photon flow (Eq. (31)), whereas for the LH model the dependence of k_{obs} on light intensity is sub-linear and displays saturation (Eq. (35)). A sub-linear dependence will be observed at relatively high light intensities such that $(k'_{25}\rho)/s_e \rightarrow k_{20}S_0$, whereas k_{obs} will be independent of photon flow at very high light intensities if $(k'_{25}\rho)/s_e \gg k_{20}S_0$.

Finally, it is worth noting that in both LH and ER mechanisms the reaction rate of photodegradation depends on the concentration of surface hydroxyl groups, $\text{OH}_{(s)}^-$. This rate depends as much on the pH of the solution as on the acid-base properties of the photocatalyst surface. Studies of the interconnection between surface acidity of metal-oxide photocatalysts and their photoreactivities are presently an active subject of our current work.

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