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Modelling of the kinetic of 2-chlorophenol catalytic photooxidation

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Abstract

The photoassisted oxidation of dilute aqueous solutions of 2-chlorophenol (2-CP) is investigated over a solid catalyst (TiO_2) at laboratory level in an annular photocatalytic reactor. In order to characterise the reaction, different kinetic models are proposed, being related to the attack of the reagent by $\cdot$OH radicals. The model based on the competitive adsorption between oxygen and 2-chlorophenol does not lead to satisfactory results. For the other models it was assumed that oxygen adsorption occurs at different sites. The model with the adsorption isotherms of reagent and oxygen being proposed of a Langmuir type is the only one able to justify the observed dependence of the pollutant disappearance rate on dissolved 2-CP concentration, oxygen partial pressure and absorbed light intensity with adsorption parameters deduced from direct measurements. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

It was stated previously that classical methods used for waste water treatment were not efficient enough. Among the pollutants refractory to degradation are chlorophenols. As representative of this class of components 2-CP was chosen. In this paper we improve the treatment of waste water using photocatalysis. At the laboratory scale the destruction of 2-CP by the UV/TiO_2/O_2 system is studied in a recirculating reactor of the immersed type with a medium pressure mercury lamp.

The aim of this paper is to propose a kinetic model for 2-CP photodegradation which represents the experiments, the adsorption parameters being deduced from direct measurements. Three kinetic models are discussed considering the influence of 2-CP concentration, of oxygen partial pressure and of absorbed light intensity in order to propose an expression of reaction rate which justifies and describes satisfactorily the experimental results.

2. Experimental

2.1. Photoreactor

Experiments were performed in a differential conversion photoreactor. The experimental apparatus consists of a 2 l cylindrical Pyrex batch tank of 100 mm internal diameter. The gas flowing through the suspension is introduced by a Teflon distributor; its flow rate is fixed at 19.4×10^{-6} m^3 s^{-1}. In addition to the agitation due to gas bubbles, the suspension was stirred mechanically and pumped (the flow rate being

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ranging from 5.5×10^{-6} to 25×10^{-6} m^3 s^{-1}) through an external recirculation loop which includes the photoreactor. This photoreactor is an annular Pyrex tube (ID: 0.03 m; OD: 0.052 m) inside which the irradiation source (HPK 125 medium pressure mercury lamp) is placed. The intensity distribution of the lamp was measured by Braun et al. [1] and the wavelength for the maximal intensity was found at 366 nm. The power emitted by this irradiation source was measured by uranyloxalate actinometry, obtaining a value of 1.98×10^{-5} Einstein l^{-1} s^{-1}. The experimental device used has already been described in detail elsewhere [2].

The adsorption of 2-CP was performed in a cylindrical Pyrex reactor of 1 l stirred with a magnetic bar. The adsorption of oxygen on TiO2 was measured by a dynamic method in a cylindrical stirred reactor of 1 l.

2.2. *Reagents*

Titanium dioxide (TiO_2) was used, provided by Degussa P25. It is in the anatase form and has a BET surface area of 50±15 m^2 g^{-1} and an average particle diameter of 30 nm. The standard grade 2-CP was purchased from Merck. All other chemicals were of reagent-grade quality and used without any further purification. The water used in the preparation of all the solutions was obtained from a Millipore Waters Milli-Q water purification system.

2.3. *Analysis*

All samples were taken using a syringe and then immediately filtered using a 0.45 mm cellulose acetate membrane (type HA Millipore).

The 2-CP concentration was measured in a Waters HPLC (510) equipped with a Nova-Pak C18 column. UV detection was performed at 254 nm, the mobile phase was 50% acetonitrile/50% water at 0.75 ml min^{-1}. The oxygen concentration was analysed using a calibrated oxygen probe.

The experiments were carried out at 25°C; the variation ranges of examined parameters are:

$$10^{-4} < C_{2\mathrm{CP}} < 6 \times 10^{-3}\,\mathrm{mol\,l^{-1}},$$

$$0 < (P_{\mathrm{O_2}})_{\mathrm{gas}} < 1\,\mathrm{atm},$$

$$0.23 \times 10^{-5} < I_{\mathrm{abs}} < 1.18 \times 10^{-5}\,\mathrm{Einstein\,l^{-1}\,s^{-1}}.$$

3. Results and discussion

3.1. *Equilibrium dark adsorption of 2-chlorophenol and oxygen*

Several kinetic models describing mechanism of photooxidation reaction have been proposed; in particular, a Langmuir–Hinshelwood law has been qualitatively proved in numerous cases of photocatalytic degradation [3]. However, a detailed description of the relation between the phenomenon of adsorption and kinetics of photooxidation could be ambiguous. In order to obtain a greater precision for the kinetic parameters of the photodegradation, we have measured independently kinetic and isotherm adsorption of 2-chlorophenol and oxygen on the TiO_2.

The 2-chlorophenol adsorption isotherm can be represented by a Langmuir adsorption type. At 25°C the adsorption constant and maximum adsorbed concentration are respectively (cf. Fig. 1):

$$K_{2\mathrm{CP}} = 3600\,\mathrm{l\,mol^{-1}},$$

$$Q_{\max} = 0.107 \times 10^{-3}\,\mathrm{mol\,g^{-1}}.$$

On the other hand, the oxygen adsorption was carried out using a dynamic method. Results show in the studied range that oxygen adsorption can be represented, both, by Langmuir and by Freundlich isotherms (Fig. 2). The Langmuir parameters are:

$$K_{\mathrm{O_2}} = 9632\,\mathrm{l\,mol^{-1}},$$

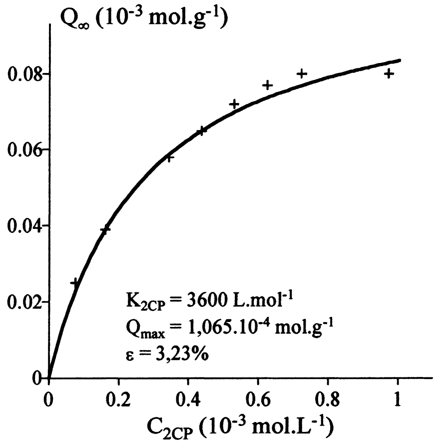

Fig. 1. Adsorption isotherm of 2-CP on TiO_2.

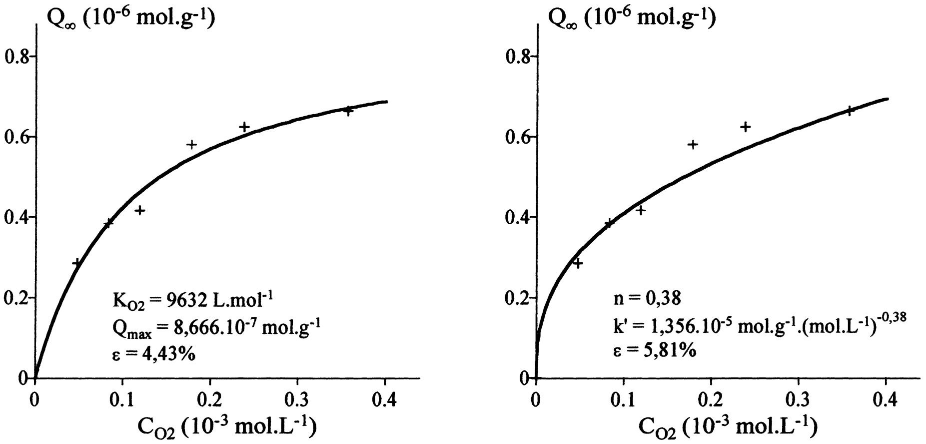

Fig. 2. Adsorption isotherms of oxygen on TiO_2: (a) Langmuir isotherm; (b) Freundlich isotherm.

$Q_{\max} = 0.87 \times 10^{-6}\,\mathrm{mol\,g^{-1}}$,

and Freundlich parameters are:

$n = 0.38$,

$k' = 1.36 \times 10^{-5}\,\mathrm{mol\,g^{-1}\,(mol\,l^{-1})^{-0.38}}$.

Differences between these two isotherms will be assessed using the results obtained by modelling of kinetic of reaction rate of 2-CP photodegradation.

3.2. Modelling of the kinetic of 2-CP photodegradation

From different elementary models proposed for photocatalytic reaction, including the presence of free hydroxyl radicals ·OH, we propose the following rate law:

$$r = k_r[C_{O_2}]_{ads}[C_{2CP}]^*_{ads}, \tag{1}$$

where k_r is the rate constant, $[C_{O_2}]_{ads}$ represents the adsorbed concentration of dissolved oxygen, $[C_{2CP}]^*_{ads}$ represents the adsorbed and activated 2-CP concentration.

The adsorbed and activated 2-CP concentration is proportional to the adsorbed radicals which is proportional to the specific absorbed light intensity I_{abs}. Consequently, the reaction rate becomes:

$$r = k_r k_I I_{abs}[C_{O_2}]_{ads}[C_{2CP}]_{ads}, \tag{2}$$

where I_{abs} is the absorbed light intensity and $[C_{2cp}]_{ads}$ the adsorbed concentration of 2-CP.

Different hypotheses can then be postulated for 2-CP and oxygen adsorption, i.e.:

- 2-CP and oxygen are adsorbed on the same sites;
- 2-CP and oxygen are adsorbed on different sites;
- 2-CP and solvent (water in our study) adsorption are competitive on the same sites.

From these hypotheses different kinetic models can be proposed to model the photodegradation rate.

The first model is based on the assumption that 2-CP and oxygen adsorption occurs on the same sites and according to a Langmuir isotherm type. The 2-CP and oxygen adsorbed concentration could be expressed as

$$[C_{2CP}]_{ads} = \frac{K_{2CP}C_{2CP}}{1 + K_{2CP}C_{2CP} + K_{O_2}C_{O_2}}, \tag{3}$$

$$[C_{O_2}]_{ads} = \frac{K_{O_2}C_{O_2}}{1 + K_{2CP}C_{2CP} + K_{O_2}C_{O_2}}, \tag{4}$$

where K_{2CP} (resp. K_{O_2}) is the equilibrium adsorption constant of 2-CP (resp. oxygen), C_{2CP} (resp. C_{O_2}) is the concentration of 2-CP (resp. oxygen) in the liquid phase.

Analysis of elementary steps leads to the rate law

$$r = \frac{k'_r I_{abs} C_{O_2} C_{2CP}}{(1 + K_{O_2}C_{O_2} + K_{2CP}C_{2CP})^2}, \tag{5}$$

where k'_r is the apparent rate constant.

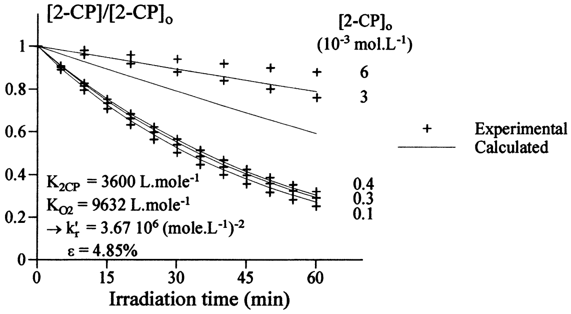

Fig. 3. *First model.* Experimental and calculated values of reduced 2-CP concentrations versus time.

Using the values of $K_{2\mathrm{CP}}$ and K_{O_2} determined from dark adsorption measurements, the parameter k_r' was evaluated by fitting the results obtained at different initial concentrations of 2-CP and is found to be $3.67\times10^6\,(\mathrm{mol\,l^{-1}})^{-2}$. The comparison of our experimental results to the model is presented in Fig. 3. The model cannot describe satisfactorily the pollutant disappearance rate, neither at the higher substrate concentrations, nor at the lower ones.

To improve reaction rate, Al-Akabi and Serpone [4] and Pelizzetti et al. [5] proposed that reaction rate should include competitive adsorption by solvent and pollutant; under this assumption, the reaction rate can be expressed as follows:

$$r = \frac{k_\mathrm{r}' I_\mathrm{abs} C_{\mathrm{O}_2} C_{2\mathrm{CP}}}{(1 + K_\mathrm{S} C_\mathrm{S} + K_{\mathrm{O}_2} C_{\mathrm{O}_2} + K_{2\mathrm{CP}} C_{2\mathrm{CP}})^2}, \tag{6}$$

where K_S is the equilibrium adsorption constant of solvent and C_S the concentration of solvent.

Moreover, to the extent that $C_\mathrm{S} > C_{2\mathrm{CP}}$ and C_S remains essentially constant, the part of surface covered by the solvent is approximately unchanged for all the reactant concentrations used. Under these conditions, Eq. (6) can be further simplified to

$$r = \frac{k_\mathrm{r}' I_\mathrm{abs} C_{\mathrm{O}_2} C_{2\mathrm{CP}}}{(K + K_{\mathrm{O}_2} C_{\mathrm{O}_2} + K_{2\mathrm{CP}} C_{2\mathrm{CP}})^2}, \tag{7}$$

where K is equal to $1+K_\mathrm{S}C_\mathrm{S}$.

The values of the parameters K and k_r' have been evaluated using the values of $K_{2\mathrm{CP}}$ and K_{O_2} determined from dark adsorption measurements. The best value of K is found to be 1 (with $k_\mathrm{r}' = 3.67\times10^6\,(\mathrm{mol\,l^{-1}})^{-2}$ and ε=4.85%) and the description of our experimental results is then not better than that with the preceding model.

The third model is based on assumption that reduction sites are different from oxidation sites. Indeed results of spin trapped technical experiments of $^{\cdot}$OH radicals formed in the photodegradation reaction, obtained by Terzian et al. [6], allowed confirmation of the existence of different adsorption sites for organic pollutant and oxygen; these authors stated that organic substrates adsorb on surface hydroxyls ($\mathrm{Ti^{IV}\text{-}OH^-}$) while molecular oxygen adsorbs onto the $\mathrm{Ti^{III}}$ sites. Taking into account the competitive adsorption between solvent and 2-CP and assuming that oxygen and 2-CP adsorptions obey a Langmuir isotherm, the reaction rate may be expressed as follows:

$$r = \frac{k_\mathrm{r}' I_\mathrm{abs} C_{\mathrm{O}_2} C_{2\mathrm{CP}}}{(1 + K_{\mathrm{O}_2} C_{\mathrm{O}_2})(K + K_{2\mathrm{CP}} C_{2\mathrm{CP}})}. \tag{8}$$

In comparison with the preceding model (cf. Fig. 4), the representation of our results (Fig. 5) seems to be improved (using as before values of $\mathrm{K_{O_2}}$ and $\mathrm{K_{2CP}}$ deduced from direct adsorption measurements). The optimized values of K and k_r' are:

$$K = 2.68, \quad k_\mathrm{r}' = 0.80\times10^5\,(\mathrm{mol\,l^{-1}})^{-2}.$$

With these values, the derived relationship (8) is able to represent very satisfactorily the observed decays of $C_{2\mathrm{CP}}$ versus time and the observed dependence of the measured kinetic constant on the dissolved oxygen concentration (Fig. 5(a)) and on the absorbed light intensity (Fig. 5(b)).

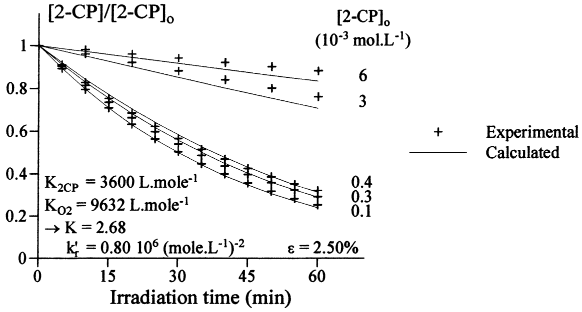

Fig. 4. *Third model.* Experimental and calculated values of reduced 2-CP concentrations versus time.

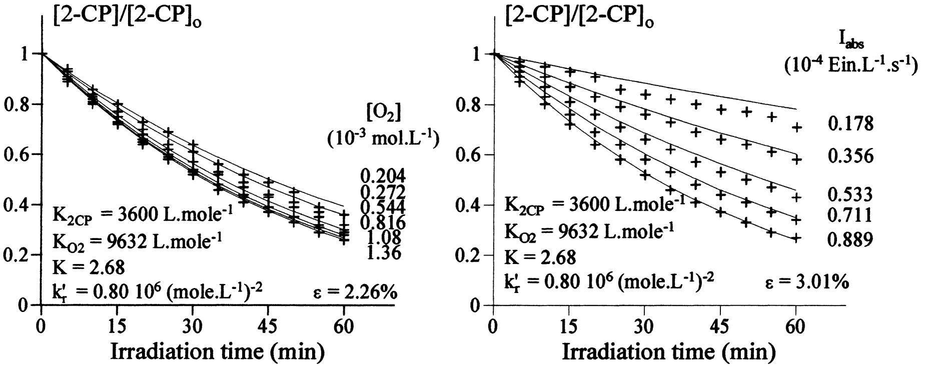

Fig. 5. *Third model.* Influence of the operating conditions: (a) oxygen concentration; (b) absorbed light intensity.

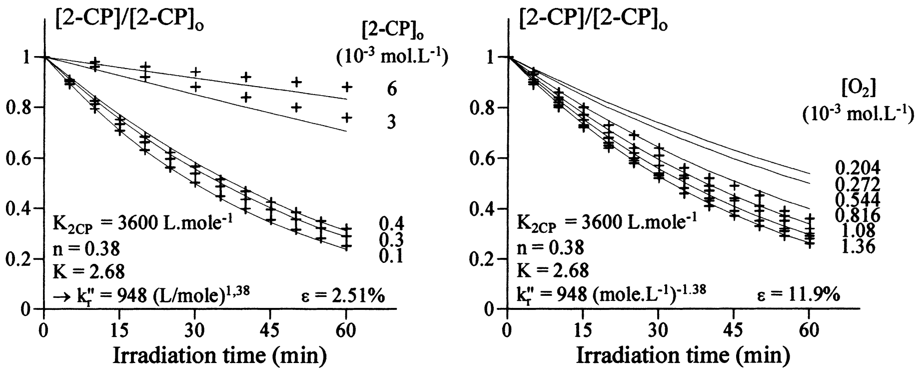

Fig. 6. *Fourth model.* Influence of the operating conditions: (a) initial 2-CP concentration; (b) oxygen concentration.

Furthermore, we tried to use the Freundlich model ($Q_{\mathrm{ads}} = kC_{\mathrm{O}_2}^{n}$) to describe the adsorption isotherm of oxygen (cf. Fig. 2). The reaction rate can then be written as follows:

$$r = \frac{k_{\mathrm{r}}'' I_{\mathrm{abs}} C_{\mathrm{O}_2}^{n} C_{2\mathrm{CP}}}{K + K_{2\mathrm{CP}} C_{2\mathrm{CP}}}. \tag{9}$$

Results obtained with this fourth model are in good agreement with the experimental data with respect with initial 2-CP concentration (Fig. 6(a)), but are very far from them if the varying parameter is the oxygen concentration (Fig. 6(b)).

In order to use the Freundlich isotherm, one should assign the value 0.2 to the exponent *n*, but the experimental adsorption values (pointed out on Fig. 2) are no longer in good agreement with the calculated ones. Therefore we cannot use the Freundlich model for oxygen adsorption; only the Langmuir model is then able to represent the whole experimental results with adsorption parameters deduced from direct and dark measurements.

4. Conclusion

This study has permitted to show that organic compounds, which are refractory to classical methods, can be degraded using a photocatalytic process.

The kinetic of 2-CP photocatalytic degradation obeys Langmuir–Hinshelwood model. 2-CP adsorption occurs in competition with that of solvent on the same sites. Therefore dissolved oxygen adsorption occurs on different sites. According to our experimental results, the adsorption isotherms of 2-CP and oxygen are of Langmuir type.

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