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Kinetics and adsorption comparative study on the photocatalytic degradation of *o*-, *m*- and *p*-cresol

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Abstract

The kinetics and adsorption aspects of the photocatalytic degradation of three cresolic isomers were studied in aqueous suspension containing TiO_2 (Degussa P-25). The Langmuir–Hinshelwood model (L–H) was applied to the kinetic results. Degradation kinetic constants were similar for the three compounds (*o*-cresol, 0.0188 ppm/s; *m*-cresol, 0.0166 ppm/s; *p*-cresol, 0.0182 ppm/s). However, the adsorption pattern of *p*-cresol is different from those of the other organics. Results from adsorption experiments carried out in darkness were modelized by using Langmuir and Freundlich isotherms. In general, the studied cresols showed little adsorption on TiO_2 surface. The adsorbed species on the catalyst surface were identified by FITR spectroscopy. According to these results, only *p*-cresol forms cresolates. An important correlation between Langmuir constants and FTIR results was observed.

Keywords: Cresol; Adsorption; Kinetics; Langmuir; Langmuir–Hinshelwood; Freundlich; FTIR

1. Introduction

In recent years, many researchers have devoted much effort to the application of photocatalysis to the elimination of different contaminants in wastewater treatments [1–3]. The photocatalytic process starts with the activation of a catalyst by radiation with higher energy than that of the band gap of the catalyst. In this case, the excited electrons are promoted from the valence to the conduction band yielding holes (h^+) and photogenerated electrons (e^-), which can act as oxidisers and reducers, respectively. The holes tend to react with substances having nucleophylic atoms, such as H_2O, OH^- and organics adsorbed onto the catalyst surface. Contrary to this, the electrons would react with electrophylic species, such as dissolved oxygen, resulting in a reduced electron–hole recombination.

Many authors have indicated that the adsorption of the substrates on the catalyst surface is a requisite for highly efficient photodegradations [4–7]. Nevertheless, not much attention has been paid to study the adsorption of contaminants on TiO_2 surface [8,9].

In this work, the adsorption and degradation aspects of the photocatalytic degradation of three cresols widely used in the fabrication of disinfectants were studied. The Langmuir–Hinshelwood classic model was applied to the kinetic results and the Langmuir and Freundlich isotherms to the adsorption results. During the adsorption experiments, the interactions between the organics and the surface of TiO_2 were studied by FTIR spectroscopy.

2. Materials and experimental conditions

The cresols (>99% purity) were supplied by Fluka. TiO_2 was Degussa P-25 (80% anatase and 20% rutile, specific surface of 50 m^2/g) [10]. H_2SO_4 (96%) and NaOH (97%) from Scharlau and Aldrich, respectively, were diluted for pH adjustment. All solutions were prepared in Milli-Q water.

2.1. Kinetic studies

All the experiments were performed in glass reactors at room temperature (20 °C). The reactors were stirred (450 rpm)

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by magnetic bars and saturated with air (Stirrer Batch Reactor, SBR). The initial pH was 5. The concentration of the catalyst was 2 g/l, as observed to be the optimal one in previous studies with other substrates.

A 60 W Solarium Philiphs HB175 equipped with four 15 W Philips CLEO fluorescent tubes with emission spectrum from 300 to 400 nm (maximum around 365 nm) was used as UV source. The lamp was located outside the reactor. To maximize the incident radiation, dihedrical reflectors were placed behind the reactor. The initial volume of the solution to be treated was 0.5 l and the irradiated surface was 384 cm^2.

All the solutions were kept in the dark for 30 min before irradiation to achieve adsorption equilibrium. Ten millilitres aliquots were sampled at different times and filtered with 0.45 μm syringe filters. At the end of the kinetic experiments, the volume was reduced by 18%, the irradiated surface was 312 cm^2, being diminished by 19%.

The remaining phenolics concentrations at different reaction times were HPLC-measured using a Macherey-Nagel CC 250/4 NUCLEOSIL 100-5 PROTECT 1 and a acetonitrile–water–acetic acid (40:59.6:0.4 vol.%) mobile phase and a UV detector ($\lambda = 270$ nm). The injected volumes remained constant as a 10 μl Rheodyne injection port-valve was used.

Changes in solution reaction volume, irradiated surface and volume of injected sample were supposed not to exert any effect on the adsorption and kinetic experiments.

2.2. Adsorption studies

Adsorption experiments were performed in darkness in a glass cylinder reactor (Trallero and Schlee) equipped with a thermostat set at 20 °C, under the same initial conditions of pH, catalyst concentration and stirring speed. Different concentrations of the cresols were tested. Once the equilibrium was achieved, samples were taken in triplicate (30 min) [11–13], filtered and analysed by HPLC as described above.

2.3. FTIR studies

A FTIR spectrophotometer model RS/1 (UNICAM) was used for spectral analysis. Spectra were obtained in the 1550–1300 cm^{-1} region, employing a resolution of 2 cm^{-1} and a forward and reverse moving mirror speed of 10 and 6.2 kHz. A catalyst suspension highly saturated with the substrate to be studied was stirred for 24 h. Then, it was filtered, dried and placed between two CaF_2 windows for the analysis. The water spectrum was subtracted from all the obtained spectra. Also, the spectra from the pure substances were obtained as reference.

3. Results and discussion

3.1. Kinetic studies

Although the Langmuir–Hinshelwood model was developed to describe gas–liquid reactions, it is widely used for liquid–solid reactions. In this model, the reaction rate is considered to be proportional to the surface fraction covered by the substrate.

$$r = -\frac{dC}{dt} = k\,\theta \tag{1}$$

In the Langmuir isotherm:

$$r = \frac{k\,K\,C}{1 + K\,C} \tag{2}$$

C is the substrate concentration (ppm) at a given time (t, seconds); K is the Langmuir–Hinshelwood adsorption equilibrium constant (ppm^{-1}) and k is the surface reaction rate constant (ppm/s).

For highly diluted solutions ($M < 10^{-3}$, $C < 108$ ppm) the term KC is negligible with respect to the unit. Thus, Eq. (2) becomes simplified as an apparent first-order equation:

$$r = k\,K\,C = k^0\,C \tag{3}$$

$$\ln\left[\frac{C}{C_0}\right] = -k^0\,t \tag{4}$$

where k^0 represents the first-order constants that include hydroxyl groups and holes attack rate coefficients and that of adsorption onto the catalyst surface.

By representing ln (C/C_0) versus t, Eq. (4) yields a straight line whose slope is k^0. Fig. 1 shows the obtained results for the three isomers.

Previous experiments showed that the catalyst load seemed not to affect *m*-cresol's degradation kinetics. However, the initial pH of the solution played an important role, being 5 the optimal value.

For a determined time, the amount of substrate degraded decreased as the initial concentration was reduced. This suggests that at high concentrations an important saturation of the catalyst active centres occurs. Contrary to the observed by Sivalingam et al. [14], no induction period, hydroxyl production without detectable degradation, was observed.

As Fig. 1 shows, the representation of ln (C/C_0) versus t yields straight lines at a determined time interval. This depends on the substrate initial concentration, probably due the fact that intermediates play an important role in the degradation kinetic, as Eq. (5) states. Before loosing linearity, the obtained degradation percentages seemed not to be dependent on the initial substrate concentration, being approximately 87% for *o*-cresol, 72% for *m*-cresol and 75% for *p*-cresol.

$$r = \frac{k\,K\,C}{1 + K\,C + \sum K_i\,C_i} \tag{5}$$

where K_i and C_i are the adsorption constant and intermediates concentrations, respectively.

Table 1 shows the obtained pseudo-first-order constants at different initial concentrations of the three cresols.

As can be observed, lower k^0 values were obtained at higher initial substrate concentrations ($k^0 \propto 1/C_0$). Moreover, the k^0 values diminish more readily at lower substrate concentrations [10]. At the catalyst surface, the molecules of the substrate are attacked by hydroxyl radicals generated at active centres. As

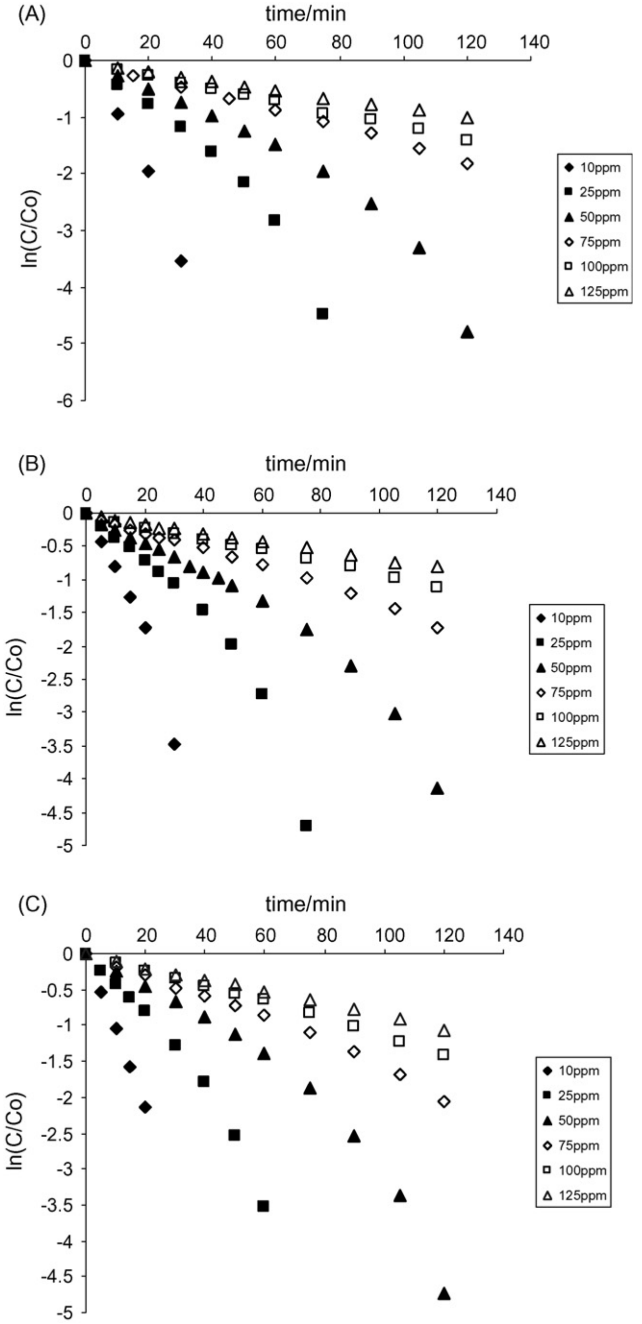

Fig. 1. Pseudo-first-order kinetics of (A) *o*-cresol, (B) *m*-cresol and (C) *p*-cresol.

the experiments were carried out in stirred reactors, the mass transfer of the substrates to the photocatalyst surface was not a determinant step. Thus, the observed k^0 diminution can be explained by the lower number of active sites due to the reduction of the initial concentration of the substrate.

The Langmuir–Hinshelwood model's rate (k) and adsorption (K) constants can be estimated by means of Eq. (2), considering initial conditions:

$$r_0 = \frac{k\,K\,C_0}{1 + K\,C_0} \tag{6}$$

Table 1
Pseudo-first-order kinetics constants, correlation coefficient (r^2) and initial rates at different initial concentrations of the three cresols

Substrate	C_0 (ppm)	k^0 ($\times 10^4$ s^{-1})	r^2	r_0 (ppm/s)
o-Cresol	10	16.1	0.999	161.0
	25	6.70	0.997	167.5
	50	4.11	0.997	205.5
	75	2.43	0.998	182.3
	100	1.98	0.996	198.0
	125	1.45	0.986	181.3
m-Cresol	10	13.8	0.999	138.0
	25	5.91	0.999	147.8
	50	3.54	0.996	177.0
	75	2.23	0.993	167.3
	100	1.57	0.996	157.0
	125	1.17	0.984	146.3
p-Cresol	10	17.3	0.9998	173.0
	25	6.99	0.997	174.8
	50	3.76	0.998	188.0
	75	2.41	0.995	180.8
	100	1.91	0.997	191.0
	125	1.47	0.997	183.8

where r_0 is the pseudo-first-order rate at the initial concentration of the substrate:

$$r_0 = k^0\,C_0 \tag{7}$$

$$k^0 = \frac{k\,K}{1 + K\,C_0} \tag{8}$$

The initial degradation rates (Eq. (7)) of *o*- and *m*-cresols became higher as their initial concentrations were increased up to 50 ppm. This could be explained by considering that at concentrations above 50 ppm, more molecules might be adsorbed on the catalyst surface resulting in a lower hydroxyl radical yield. This behaviour was not clearly observed for *p*-cresol. In any case, the majority of authors prefer to consider degradation rates as a function of the percentage of substrate degraded at a given time [11,14,15].

The kinetic and adsorption constants can be determined by applying a non-linear fitting of Eq. (8) to the data shown in Table 1. The obtained results are shown in Table 2. The determination of the kinetic constant by means of non-linear fitting generates less statistical noise [16] than that of the linearization of Eq. (8) used by other authors [8].

Table 2
Fitting parameters as determined by non-linear regression

	$a = kK$ (s^{-1})	K (ppm^{-1})	r^2	k (ppm/s)
o-Cresol	0.0109	0.579067	0.999	0.0188
m-Cresol	0.0080	0.48085	0.999	0.0166
p-Cresol	0.0309	1.69474	1.000	0.0182

Considering the kinetics constants obtained, it seems that there were no significant differences in their degradation. However, their adsorption constants are significantly different, being that of *p*-cresol about three times higher than those of the other compounds. This reveals the higher affinity of *p*-cresol for the catalyst surface. It must be stressed that the cresols show notably lower adsorptions in comparison with other aromatic compounds, such as resorcinol, catechol and phenol [17], although the degradations of the cresols are faster. The adsorption is considered to be by many authors an unavoidable step in photocatalytic degradation mechanisms. However, Parra et al. [18] have indicated that adsorption extension is not always decisive in the photocatalytic process. In addition to this, other factors can affect the kinetics of photocatalytic degradation. Two examples can be found in the nature of the adsorption centres, which could inhibit active centres [17] and the type and distribution of substituents in the chemical structure of the substrate. The adsorbed molecules can be oxidised, directly by the photogenerated holes or indirectly by the hydroxyl radicals. Interestingly, hydroxyl radicals can also oxidise substrate molecules in the bulk solution [11]. Consequently, the role of adsorption in photocatalytic degradation is uncertain. Though some authors claim that if the Langmuir–Hinshelwood model can be applied, adsorption is a prerequisite for degradation, in recent years, it has been shown that the model is quantitatively consistent for mechanisms in which oxidation occurs on the catalyst surface or in homogeneous processes [19].

3.2. Adsorption studies

Adsorption can be quantified by isotherms, which basically indicate the mass of substrate adsorbed (adsorbate) by a known mass of adsorbent, TiO_2 in our case, in equilibrium conditions. The following equation was used in these studies [20]:

$$q_e = \frac{C_0 - C_e}{m} V \tag{9}$$

where C_0 is the adsorptive initial concentration, C_e is the concentration of adsorbate in the equilibrium, m is the catalyst mass and V is the solution volume.

Ksibi et al. [15] claim that the low adsorption of aromatic compounds is caused by their solvatation by water molecules. Their adsorption on TiO_2 surface implies the break of that hydratation layer and the consequent reorganization of the involved water molecules.

The Langmuir and Freundlich isotherms are commonly used to describe adsorption in aqueous solutions.

3.3. Langmuir

This model assumes that the adsorption energy is uniform in the whole surface; there is no transmigration in the surface plane and there is no interaction between the adsorbed species. Additionally, only chemical interactions are considered. Thus, only monolayers of the adsorbate can be formed on the surface of the adsorbent. The following equation was used:

$$q_e = \frac{Q_0 \, b \, C_e}{1 + b \, C_e} \tag{10}$$

where q_e is the adsorbed mass by each gram of TiO_2, b is the Langmuir equilibrium constant, Q_0 is the maximum adsorption mass of the adsorbate that can be adsorbed on TiO_2, C_e is the adsorbate concentration in the equilibrium.

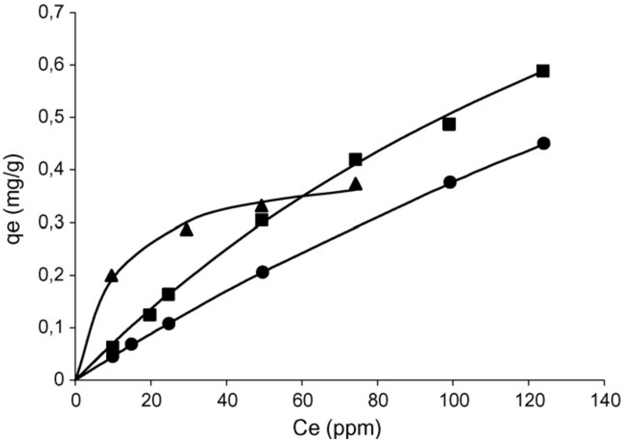

Fig. 2. Langmuir's adsorption isotherms for (●) *o*-cresol; (■) *m*-cresol and (▲) *p*-cresol.

The experimental values of q_e and C_e were fitted by means of a non-linear regression of Eq. (10). Others authors have suggested the linearized equation [9,21]. Fig. 2 shows Langmuir isotherms from the obtained adsorption results for the studied cresols.

The values of non-linear fitting parameters and the upper limit of the concentration of the substrate are shown in Table 3. The adsorption constant becomes higher in the series *o*-cresol < *m*-cresol < *p*-cresol, while the value required to saturate the catalyst surface follows: *p*-cresol < *m*-cresol < *o*-cresol. This is in agreement with the mathematical form of Eq. (10).

3.4. Freundlich

This model does not assume energetic equivalence among the adsorption centres and it can be expressed by the following equation:

$$q_e = K_F \, C_e^{1/n} \tag{11}$$

Table 3
Non-linear fitting parameters of the Langmuir (Eq. (10)) and Freundlich (Eq. (11)) isotherms

Langmuir isotherm

Substrate	Upper concentration (ppm)	$Q_0 \times b$	b (l/mg)	r^2	Q_0 (mg/g)
o-Cresol	125	0.0046	0.0022	1.000	2.105
m-Cresol	125	0.0074	0.0045	0.999	1.624
p-Cresol	75	0.0365	0.0874	0.986	0.417

Freundlich isotherm

Substrate	Upper concentration (ppm)	K_F (l/mg)	n	r^2
o-Cresol	150	0.0052	1.059	0.996
m-Cresol	150	0.0088	1.127	0.994
p-Cresol	75	0.0793	2.745	0.982

where q_e is the mass of substrate adsorbed by each gram of TiO_2, C_e is the equilibrium concentration of the substrate, K_F and n are constants related to the ability and intensity of the adsorption, respectively.

Eq. (11) can be linearized by applying logarithmic:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (12)$$

By representing $\log q_e$ versus $\log C_e$, a straight line must be obtained, from which n and K_F can be calculated. The values of K_F, n and r^2 (correlation coefficient) are shown in Table 3.

The concentration upper limit for the application of the Freundlich model is of paramount importance, as at higher concentrations, irreproducible equilibrium concentrations are measured [4]. The parameter n is related to the adsorption

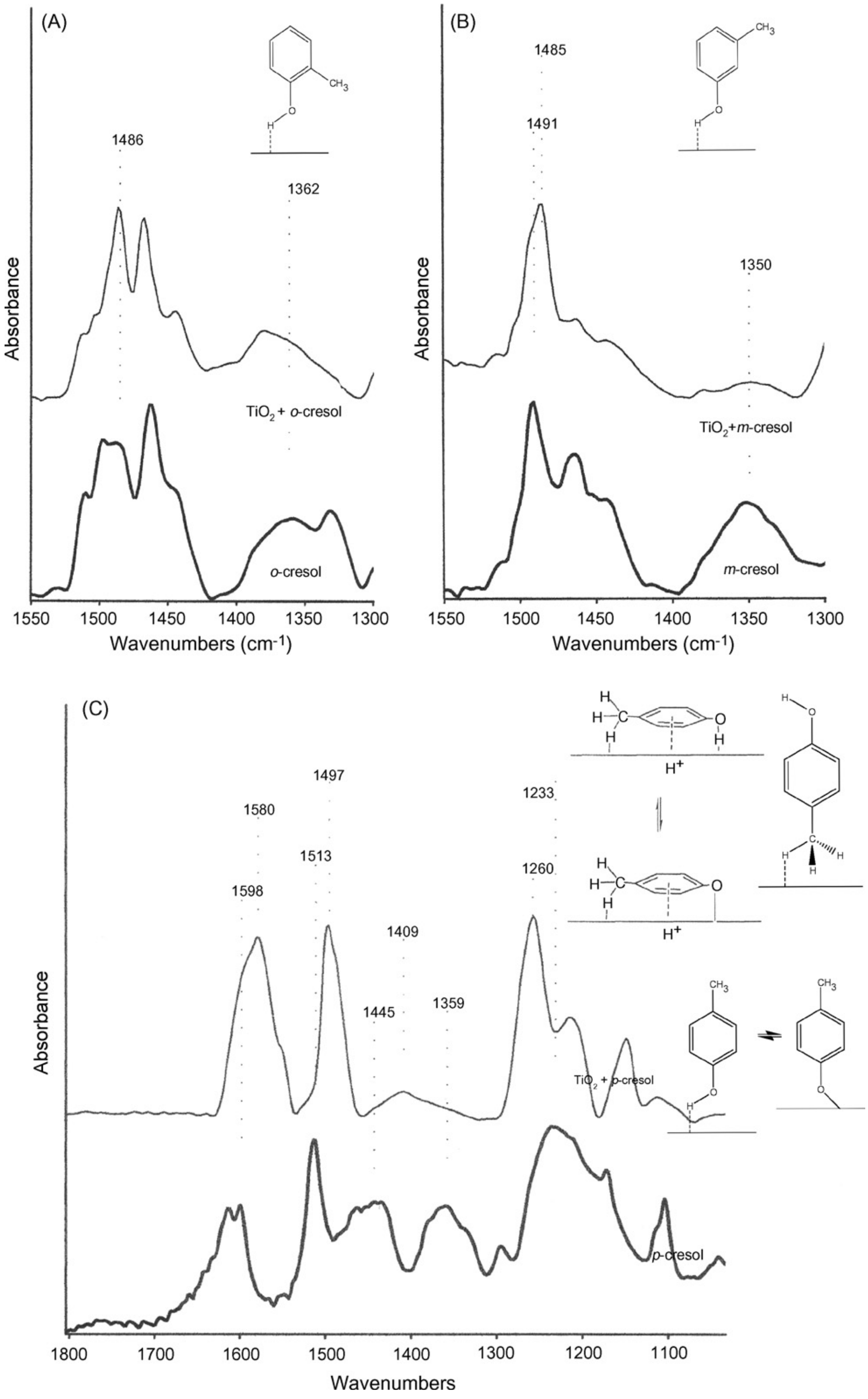

Fig. 3. FTIR spectra from the adsorption of the cresols on the TiO_2 surface. (A) *o*-cresol, (B) *m*-cresol and (C) *p*-cresol.

energy. Higher values than 1 indicate a strong TiO_2–substrate interaction, which is the case of *p*-cresol. Contrary to this, *n* values from experiments with *m*- and *o*-cresol are close to the unit, suggesting energetic similarity of the adsorption sites of these substrates and yielding a good fitting of the Langmuir isotherm for these substances. These considerations are reinforced by the notably higher value of the Freundlich's constant K_F of *p*-cresol, which indicates stronger adsorption.

According to the high values of the correlation coefficients, it can be considered that both models can describe the adsorption of these substrates on TiO_2 surface, although the fitting of *p*-cresol results is limited to lower concentrations than those of the other cresols. Additionally, both models provide convergent results.

Stafford et al. [7] have proposed a multilayer model for gas–solid interactions of 4-chlorophenol with TiO_2 (Degussa P-25). In this model, the classical monolayer formed in the adsorption equilibrium at low concentrations evolves to yield a multilayer, in which both chemisorption and physisorption occurs. This model was already suggested by Robert et al. [4] to explain the liquid-solid pattern of phenolic derivatives.

According to Mills and Hunte [22], the Langmuir adsorption constants, *K*, and those obtained with the Langmuir–Hinshelwood model are not equivalent, as lower values are usually obtained with the former [11]. Nonetheless, Valente et al. [8] did not obtained similar results. Most authors explain these differences by considering that under radiation, the electrons redistribution could affect the substrate–catalyst surface interaction, and the possible retention of the generated intermediates on the catalyst surface.

3.5. FTIR studies

Fig. 3 shows FTIR spectra from each cresol and their interaction with TiO_2, as well. The 1550–1300 cm^{-1} region is particularly interesting due to the presence of ν (C=C) and δ (OH) vibration bands. The variation or disappearance of the latter reveals the sort of interaction of the compound with the catalyst surface, i.e., by means of hydrogen bond or by forming a cresolate [7,23]. Additionally, a shift of the first component of the ν (C=C) vibration band towards higher wavenumbers would reveal a higher electrodonation to the aromatic ring [23].

It has been described that *o*- and *m*-cresols interact by means of H bonds [17]. In the case of *o*-cresol, there is an important reduction of the δ OH (1362 cm^{-1}) band intensity, but the electrodonation is not altered as suggested by the unmodifiedν C=C (1486 cm^{-1}) band. In the spectrum from *m*-cresol–TiO_2 interaction, not only the δ OH (1350 cm^{-1}) band intensity is notably reduced, but the ν C=C band is shifted from 1491 to 1485 cm^{-1}, indicating a small electrodonation diminution.

Results from *p*-cresol are different. In this case, both the δ OH (1359 cm^{-1}) band intensity and that of ν CH_3 (1445 cm^{-1}) are decreased. Moreover, the ν C=C band is notably shifted from 1513 to 1497 cm^{-1}, indicating a significantly electrodonation reduction. Additionally, the ν C–O band shift from 1233 to 1260 cm^{-1} reveals that the interaction is strong [7]. According to these results, it can be suggested that some molecules of *p*-cresol could be interacting through a resonant structure between a cresolate and an OH hydrogen bond. Other molecules could be interacting by means of an H bond of the methyl group. It is also possible that a molecule could interact through both sorts of interactions. In this last case, the aromatic ring of *p*-cresol molecules would be placed parallel to the TiO_2 surface, as indicated for *p*-nitrophenol [4]. This does not deny the possibility of the production of intermediates resulting from the methyl group oxidation in the photocatalytic degradation of *p*-cresol, as occurs with *m*- and *o*-cresol.

4. Conclusions

Results obtained in this work indicate that:

- The three aromatic isomers studied showed similar photocatalytic degradation kinetics: 0.0188, 0.0166 and 0.0182 ppm/s, for *o*-, *m*- and *p*-cresols, respectively.
- FTIR spectra indicated that the adsorption of *p*-cresol is markedly different from those of the other cresols, probably provided by the formation of a strong interaction through a resonant structure between a cresolate and an OH hydrogen bond. The other cresols interact by means of H bond.
- Adsorption studies in the darkness using two different models, Langmuir and Freundlich, confirmed the particular adsorption behaviour of *p*-cresol.
- The obtained value of Q_0 from the Langmuir model for *p*-cresol was notably higher than for the other compounds. Additionally, the Freundlich parameter related with the adsorption energy was markedly higher than the unit.
- Although *p*-cresol adsorption is clearly different from that of the other cresols, no differences in its degradation kinetics were observed. This can be explained by considering that the three compounds are located at surface active centres with similar characteristics.

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References

[1] A.G. Rincón, C. Pulgarin, Appl. Catal. B: Environ. 63 (2006) 221–231.

[2] O. Legrini, E. Oliveros, A.M. Braun, Chem. Rev. 93 (1993) 671–698.

[3] J.M. Herrmann, J. Disdier, P. Pichat, S. Malato, J. Blanco, Appl. Catal. B: Environ. 17 (1998) 15–23.

[4] D. Robert, S. Parra, C. Pulgarin, A. Krzton, J.V. Weber, Appl. Surf. Sci. 167 (2000) 51–58.

[5] H.Y. Chen, O. Zahraa, M.J. Bouchy, J. Photochem. Photobiol. A: Chem. 108 (1997) 37–44.

[6] J.M. Hermann, P. Pichat, J. Chem. Soc., Faraday Trans. I 76 (1980) 1138–1146.

[7] U. Stafford, P.V. Gray, A. Kamat, A. Varma, Chem. Phys. Lett. 205 (1993) 55.

[8] J.P.S. Valente, P.M. Padilla, A.O. Florentino, Chemosphere 64 (2006) 1128–1133.
[9] S. Bekkouche, N. Boouhelassa, N. Hadj Salah, F.Z. Meghlaoui, Desalination 166 (2004) 355–362.
[10] A. Hatipoglu, N. San, Z. Cinar, J. Photochem. Photobiol. A: Chem. 165 (2004) 119–129.
[11] E. Kusvuran, A. Samil, O.M. Atanur, O. Erbatur, Appl. Catal. B: Environ. 58 (2005) 211–216.
[12] J. Matos, J. Laine, J.M. Hermann, Appl. Catal. B: Environ. 18 (1998) 281–291.
[13] J.M. Hermann, Catal. Today 53 (1993) 115–129.
[14] G. Sivalingam, M.H. Priya, G. Madras, Appl. Catal. B: Environ. 51 (2004) 67–76.
[15] M. Ksibi, A. Zemzemi, R. Boukchina, J. Photochem. Photobiol. A: Chem. 159 (2003) 61–70.
[16] H. Motulsky, The Graphpad Guide to Nonlinear Regression, Graphpad Software Inc., 1996.
[17] J. Araña, E. Pulido Melián, V.M. Rodríguez López, A. Peña Alonso, J.M. Doña Rodríguez, O. González Díaz, J. Hazard. Mater. 146 (2007) 520–528.
[18] S. Parra, J. Olivero, C. Pulgarin, Appl. Catal. B: Environ. 36 (2002) 75–85.
[19] C.S. Turchi, D.F. Ollis, J. Catal. 122 (1990) 178–192.
[20] F.P. Hansen, R.P. Graig, J. Phys. Chem. 58 (1954) 212.
[21] V.K. Grupta, C.K. Jain, I. Ali, M. Sharma, V.K. Sain, Water Res. 37 (2003) 4038–4044.
[22] A. Mills, S.L. Hunte, J. Photochem. Photobiol. A: Chem. 108 (1997) 1–35.
[23] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, Inc., 1973.