

Photocatalytic degradability of substituted phenols over UV irradiated TiO₂

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Abstract

Synthetic wastewaters consist of substituted phenols: two hydroxyphenol (hydroquinone (hydro) and resorcinol), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP) and 2,4,6-trinitrophenol (2,4,6-TNP) were photocatalytically degraded in aqueous TiO₂ suspension. The influence of the nature of the substituent on the photodegradation has been investigated by comparing the initial degradation rates (v_0 relative to phenol) to the different substituted phenols. This reactivity follows Hammett law with regard to the effect of nature group on phenolic functionality. The plot of $v_0 = f(\sigma)$ shows a poor correlation when considering all the substituted phenols, when the nitrophenols (NO₂ substituents) are evaluated separately and the hydroxyphenol (OH substituent) is not taken into account, good correlations are observed in both groups of data. A considerably influence of pH upon the kinetics of chemical oxygen demand (COD) disappearance was observed. In general, acidic pH is preferred to COD removal for all phenolic compounds. Photocatalysis transforms the nitro group in nitrophenols into NO₃⁻ and NH₄⁺ through the formation of NO₂⁻ intermediate. The amount of nitrate depends on the number of nitro group in nitrophenol. The selectivity in nitrate ions is equal to 80, 56 and 66%, respectively, for 4-NP, 2,4-DNP and 2,4,6-TNP. It was also found that all the photo-treated solutions which we evaluated the ratios 5-day biological oxygen demand (BOD₅)/COD show values higher than those recorded in initial solutions which is an indication of the positive effect of the applied photo-treatment.

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1. Introduction

Phenolic compounds pose a significant treat to the environment. They are commonly found in industrial effluents and have been detected in urban and agricultural waste. Nitrophenolic compounds, for example, are released into the environment through their wide use as dyes, pesticides, plasticizers, and solvents. It is reported that some monitrophenol can be formed as degradation product of herbicide nitrofen when it is exposed to sunlight [1]. Resorcinol is used in the manufacture of adhesives and dyes and as an ingredient in pharmaceutical preparations for the topical treatment of skin conditions. The interest in phenolic compounds is their selection by the US Environmental Protection Agency as persistent, bioaccumulative, and toxic (PBT) chemicals [2].

The photocatalytic degradation of these toxic compounds in aqueous medium provides a new method for wastewater treatment. It has several advantages over conventional

oxidation processes such as the complete mineralization of pollutant, the utilization of near-UV light and no addition of chemicals. A quasi-exhaustive list of various families of organic pollutants, which can be treated by photocatalysis, has been given in [3]. In most cases, the degradation is conducted for dissolved compounds in water with UV-illuminated titania. The possible extents of the technique concern the irradiation source and the physical state of the pollutant. Recently, some works have reported that the degradation of organic compounds is induced by visible light and photosensitization [4–7]. The great interest is to use solar light, which is free and inexhaustible.

The photocatalytic degradation rate of different organic compounds depends on various parameters, such as temperature, pH, and initial concentration of the pollutant, photocatalyst loading, light intensity and chemical structure of the reactor, among others. In this paper, special attention is given to the effect of the structure and consequently of some physicochemical properties of different compounds on their photoreactivity in aqueous TiO₂ suspensions. The photocatalytic degradability of some substituted

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phenols (hydroquinone (hydro) and resorcinol), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP) and 2,4,6-trinitrophenol (2,4,6-TNP) have been principally correlated to the Hammett constant(s). This one represents the effect, which different substituents have on the electronic character of a given aromatic system.

Preliminary photocatalytic oxidation experiments were performed over UV irradiated TiO₂ in order to compare the photocatalytic degradability of these substituted phenols in terms of the kinetic parameters of DCO removal in water and the impact on the biodegradation of pollutants.

2. Experimental

All substituted phenols were purchased from Fluka and used as received without further purification. Solutions were prepared using bidistilled water. Degussa P-25 titanium dioxide was used as photocatalyst. It is mostly in anatase form and has a BET surface area of 50 m² g⁻¹. A Pyrex reactor open to air was utilized. It was equipped with a plunging tube containing the same Philips HPK 125 W lamp. The tube had a Pyrex cylindrical jacket in which water was circulated to avoid the heating of the solution. The intensity of the UV-radiation reaching the reactor ($\lambda > 290$ nm) delivered an efficient photonic flux equal to 6.67×10^{-7} einstein s⁻¹. A volume of 1000 ml of solution and 1 g of TiO₂ were used. The degradations were carried out at 293 K and at different pHs. The pH was adjusted using either NaOH or HNO₃. The suspension was first stirred in the dark for 40 min before irradiation. This was sufficient to reach an equilibrated adsorption as deduced from the steady-state concentrations. To determine the adsorption constants k , different concentrations of each substituted phenol were used. Before analysis, the aqueous samples were filtered through 0.45 μ m membrane filter to remove TiO₂ agglomerates in suspension. A "HACH-4000" UV-Vis spectrometer recording the spectra over the 190–750 nm range was used for the determination of phenols concentrations to follow its kinetics of disappearance. Calibration plots based on Beer–Lambert's law were established relating the absorbency to the concentration. The molar extinction coefficients for phenol, hydroquinone, resorcinol, 4-nitrophenol, 2,4-dinitrophenol and 2,4,6-trinitrophenol were estimated at 269, 246, 274, 318, 258 and 358 nm, respectively.

Nitrite and nitrate ions formed as a result of nitrogen mineralization in nitrophenols were analyzed using HACH methods (2610 and 8037) based on diazonium salts formation. The absorbencies are proportional to ion quantity in each solution. Ammonium was analyzed according to Kjeldahl method.

The chemical oxygen demand (COD) was determined by using a Bioblock (BOD) analyzer based on the method of acidic oxidation by dichromate. The initial and treated solutions of different phenols were analyzed to measure the

5-day biological oxygen demand (BOD₅). This one was determined by using the HACH BODTrakTM method.

3. Results and discussion

3.1. Adsorption of the phenols on titania

The kinetic of adsorption for the six phenolic compounds (phenol, resorcinol, hydroquinone, 4-NP, 2,4-DNP and 2,4,6-TNP) are represented in Fig. 1 for different initial concentrations varying between 5 and 30 ppm indicated on the right side of every curve. It can be observed that whatever be the phenolic compound and its initial concentration, the steady state of adsorption is reached within 40 min. Therefore, this time has been selected for the initial period in the dark previously to UV-irradiation at time $t_{UV} = 0$ to make sure that the initial degradation initiates at the equilibrium of adsorption. The different values of the quantities adsorbed at the steady state have been depicted in a Langmuirian plot $1/n_{ads} = f(1/C_e)$ (Fig. 2). The linearity of the transforms indicates clearly that the Langmuir isotherm is correctly observed, implying a monolayer adsorption model. From the data in Figs. 1 and 2, we could determine the maximal quantities q_{max} in mol g_{cat}⁻¹ of adsorbed phenolic compounds, the adsorption constants k_{ads} , and the areal density of adsorbed phenolic molecule in mol nm⁻² (the adjective "areal" refers to the a surface area unit, as defined by Burwell in the IUPAC return in [8]). These values are reported in Table 1.

The adsorption constants k_{ads} , vary from 1.45×10^3 to 31×10^3 l mol⁻¹. The higher value concerns that of 2,4-DNP. This can be attributed to the *ortho*-position of nitro ($-NO_2$) group in the aromatic ring. On the other hand, the weakest adsorption constant interests the 2,4,6-TNP. It can be explained by the big geometric hindrance due to the big number of nitro groups on the aromatic ring. The areal coverages are given in the last column in Table 1. They vary between 0.006 and 0.065 mol nm⁻².

The number of molecules effectively adsorbed indicates a low coverage. This phenomenon results from the adsorption of solvated molecules. Pollutant molecules are needed to break the H₂O tridimensional net at TiO₂ surface and to

Table 1
Adsorption characteristics of phenolic compounds

Compound	q_{max} (μ mol g ⁻¹)	$k_{ads} \times 10^{-3}$ (l μ mol ⁻¹)	n_{ads} (mol nm ⁻²)
2,4,6-TNP	5.44	1.45	0.065
Hydroquinone	2.33	25	0.028
2,4-DNP	1.31	31	0.0158
Resorcinol	1.12	3.3	0.013
Phenol	0.95	11	0.01
4-NP	0.55	20.6	0.006

q_{max} , maximum quantities adsorbed per g_{cat}; k_{ads} , adsorption constants; n_{ads} , areal density of adsorbed phenolic molecules (in mol nm⁻²).

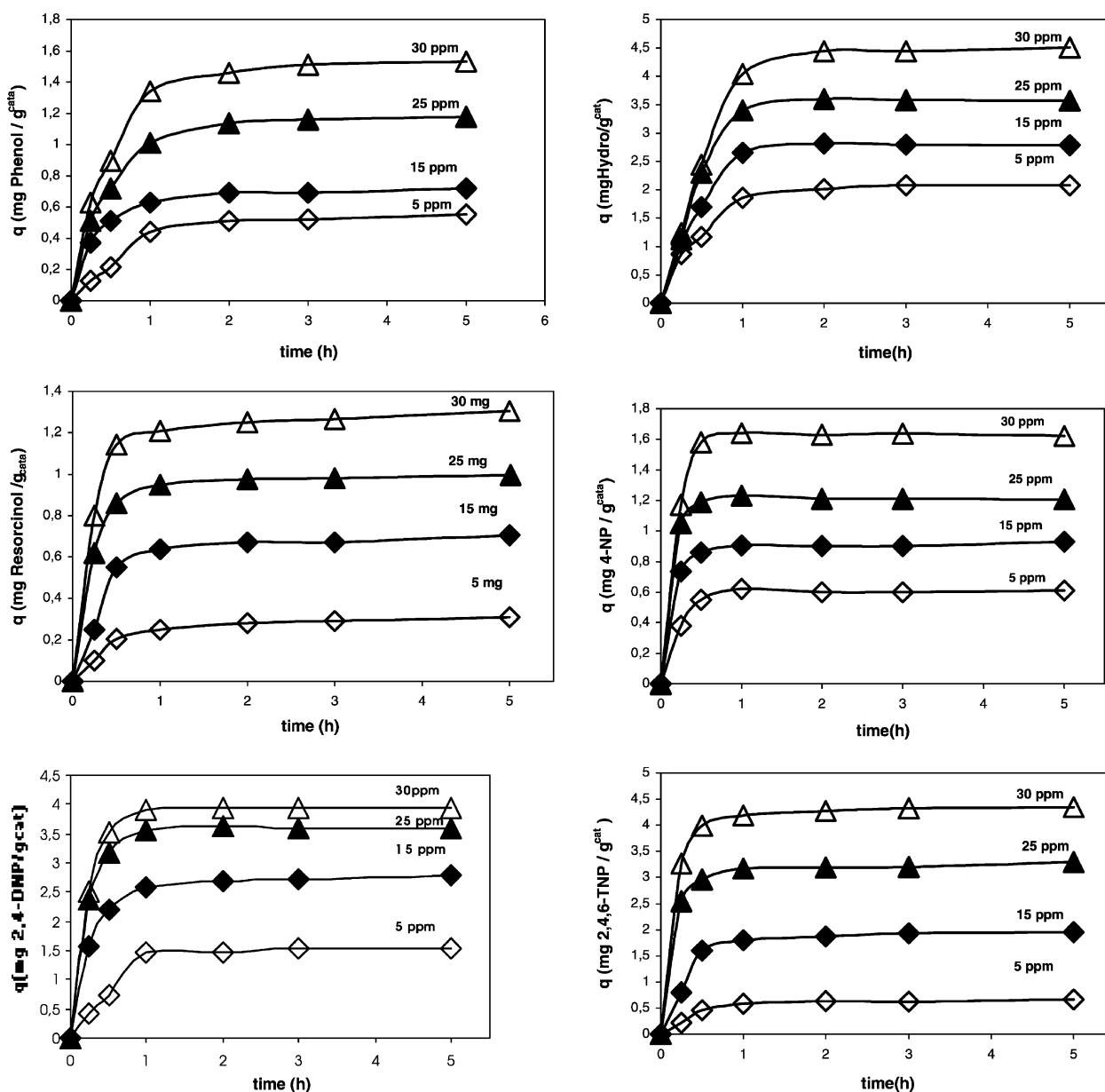


Fig. 1. Kinetics of adsorption of phenolic compounds. Experimental conditions: $C_0 = 175 \mu\text{mol l}^{-1}$; $m(\text{TiO}_2) = 50 \text{ mg}$; $V = 50 \text{ ml}$; $T = 30^\circ\text{C}$; natural pHs.

reorganize the water molecules around them. This creates difficult thermodynamic changes, which also depend on their localization (monolayer or bulk). The number of adsorbed molecules decreases in the order: 2,4,6-TNP > Hydro > 2,4-DNP > resorcinol > phenol > 4-NP.

3.2. Photocatalytic degradation of the six phenolic compounds

After checking that no detectable degradation occurred without titania nor UV-irradiation, the photocatalytic disappearance of the six phenolic compounds is performed according to the procedure indicated in the experimental section. The kinetics are given in Fig. 3. All reactions

follow an apparent first-order verified by the linear transforms $\ln C_0/C = f(t)$ illustrated in the insert of Fig. 3. The slopes give the apparent rate constants listed in Table 2.

3.2.1. Influence of the substituents on degradability

The influence of the substituent nature on the photodegradation of substituted phenols is investigated by comparing their initial rates of degradation (v_0), which is the decay of the phenolic compound concentration after 10 min of the photoreaction. In the various experiments carried out, the initial concentration in phenolic compound (C_0) = $175 \mu\text{mol l}^{-1}$ and the concentration of $\text{TiO}_2 = 1 \text{ g l}^{-1}$. The first column in Table 2 presents the initial degradation rates for these substituted phenols. These values are calculated

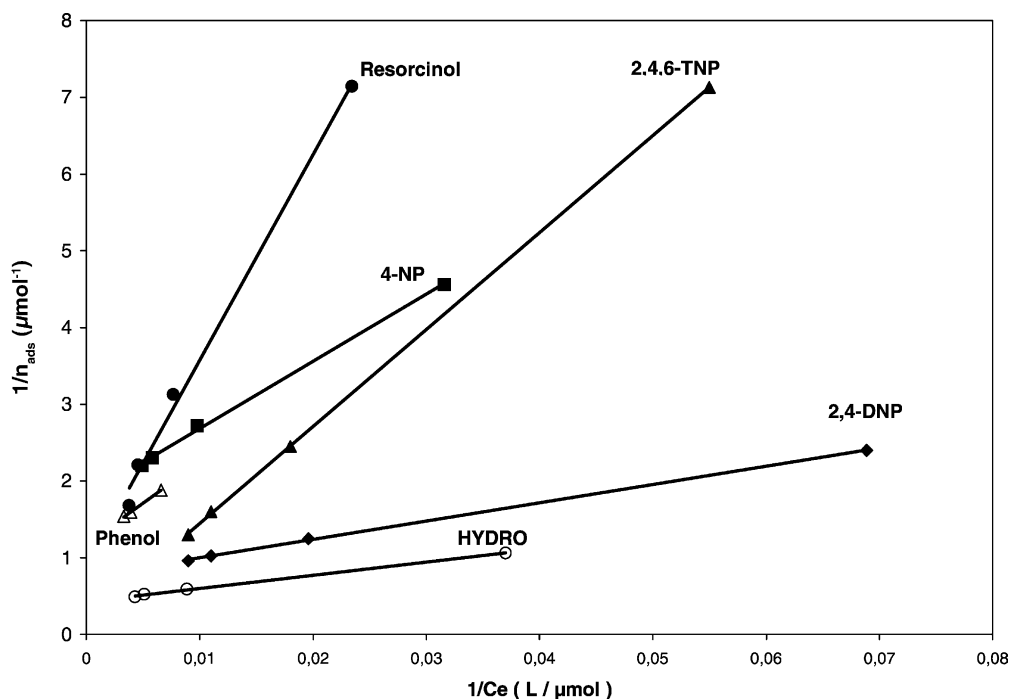


Fig. 2. Linear transforms of Langmuir isotherms deduced from results in Fig. 1. Conditions: $C_0 = 175 \mu\text{mol l}^{-1}$; $m(\text{TiO}_2) = 50 \text{ mg}$; $V = 50 \text{ ml}$; $T = 30^\circ\text{C}$; natural pHs.

and compared to the phenol, which is regarded as a reference compound. The last column in Table 2 presents the literature Hammett constant (σ) for each compound. Hammett constant (σ) of polynitrophenol was calculated as a sum of

σ 's of nitro groups, adopting the values 0.71, 0.78 and 1.24, respectively, for *meta*-, *para*- and *ortho*-positions [9,10].

The Hammett constant represents the effect that the various substituents have on the electronic character of a

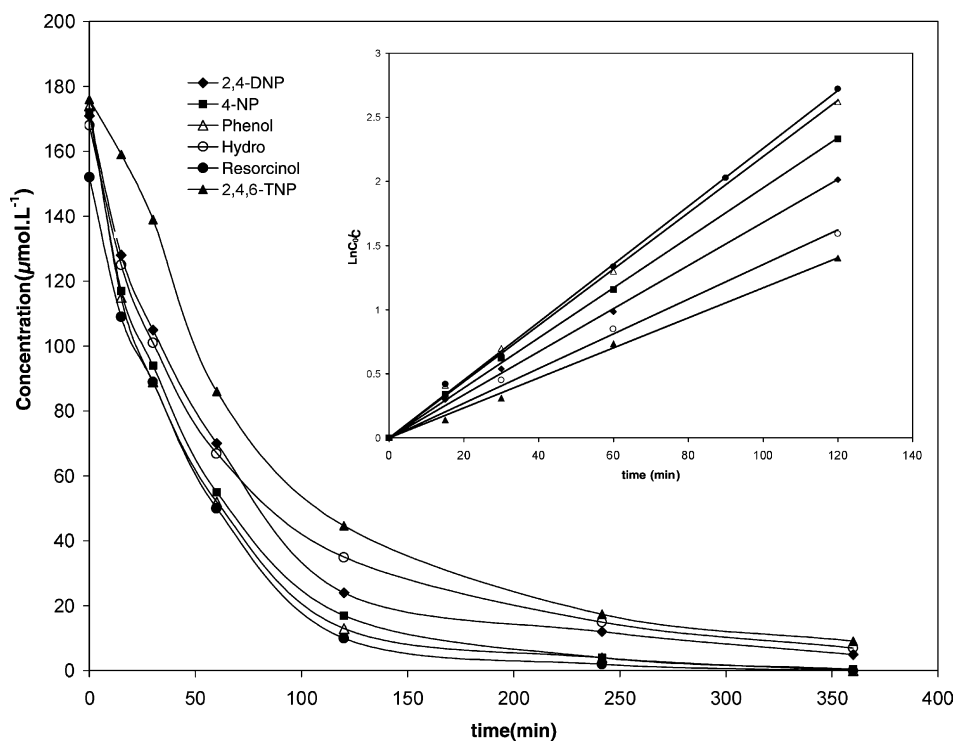


Fig. 3. Kinetics of the photocatalytic degradation of the phenols. First-order linear transform $\ln C_0/C = f(t)$ (insect). Conditions: $C_0 = 175 \mu\text{mol l}^{-1}$; $m(\text{TiO}_2) = 1 \text{ g}$; $V = 1000 \text{ ml}$; $T = 30^\circ\text{C}$; natural pHs.

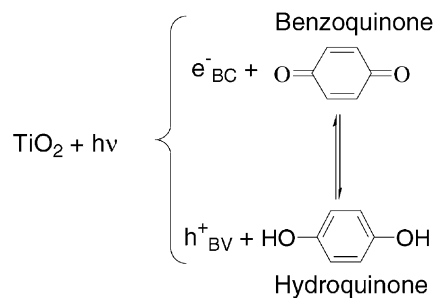
Table 2
Initial photodegradation rates (v_0) and first-order rate constants (k) relative to phenol for the abatement of substituted phenols

Compound	v_0 (relative to phenol)	k (mn ⁻¹)	σ
4-NP	0.89	0.0195	0.78
2,4-DNP	0.76	0.0168	2.02
2,4,6-TNP	0.53	0.0117	3.26
Resorcinol	1.03	0.0226	0.1
Hydroquinone	0.61	0.0135	-0.38
Phenol	1	0.0219	0

Unsubstituted phenol is used as reference compound.

given aromatic system [10]. A positive value indicates an electron-withdrawing group while a negative value indicates that of the electro-donor group. Hammett constants are then employed to establish a correlation with initial degradation rates for substituted phenols (Fig. 4). Although the plot of $v_0 = f(\sigma)$ shows a poor correlation when considering all the substituted phenols, when the nitrophenols are evaluated separately and the hydroxyphenol (OH substituent) is not taken into account, good correlations are observed in both groups of data. The nitrophenols exhibit a different behavior probably due to the electronegative character.

Hydroquinone, having two groups strongly activator, is not the most reactive among the studied compounds. It was reported [11] that the low speed of hydroquinone decomposition could be related to a keto-enolic oxydo-reductive tautomeric effect as illustrated in Scheme 1. Due to this effect, the oxidation of hydroquinone to benzoquinone by photo-



Scheme 1.

generated holes (h^+) formed in the valence band of the TiO_2 semiconductor can be followed by the capture of an electron of the band of conduction by the benzoquinone, giving place to a reaction of recombination.

3.3. Kinetics of total mineralization of the six phenolic compounds

The kinetics of the total mineralization of the six substituted phenols has been followed by the disappearance of the COD. This technique is well used for expressing the detoxification level of water.

3.3.1. Kinetics of COD disappearance

The kinetic isotherms of COD disappearance are given in Fig. 5. For all the six phenols, a high COD reduction (greater than 90%) is also achieved. The initial values plotted in the

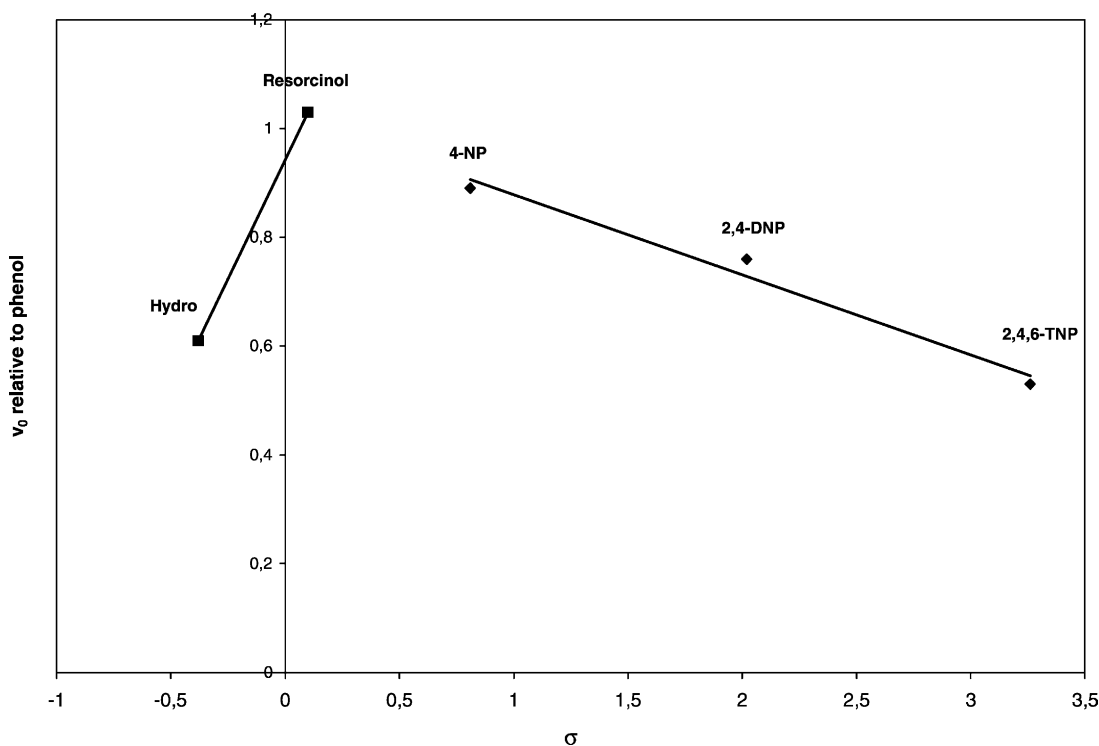


Fig. 4. Relationship between the initial degradation rate (v_0) and Hammett constants (σ) of substituted phenols.

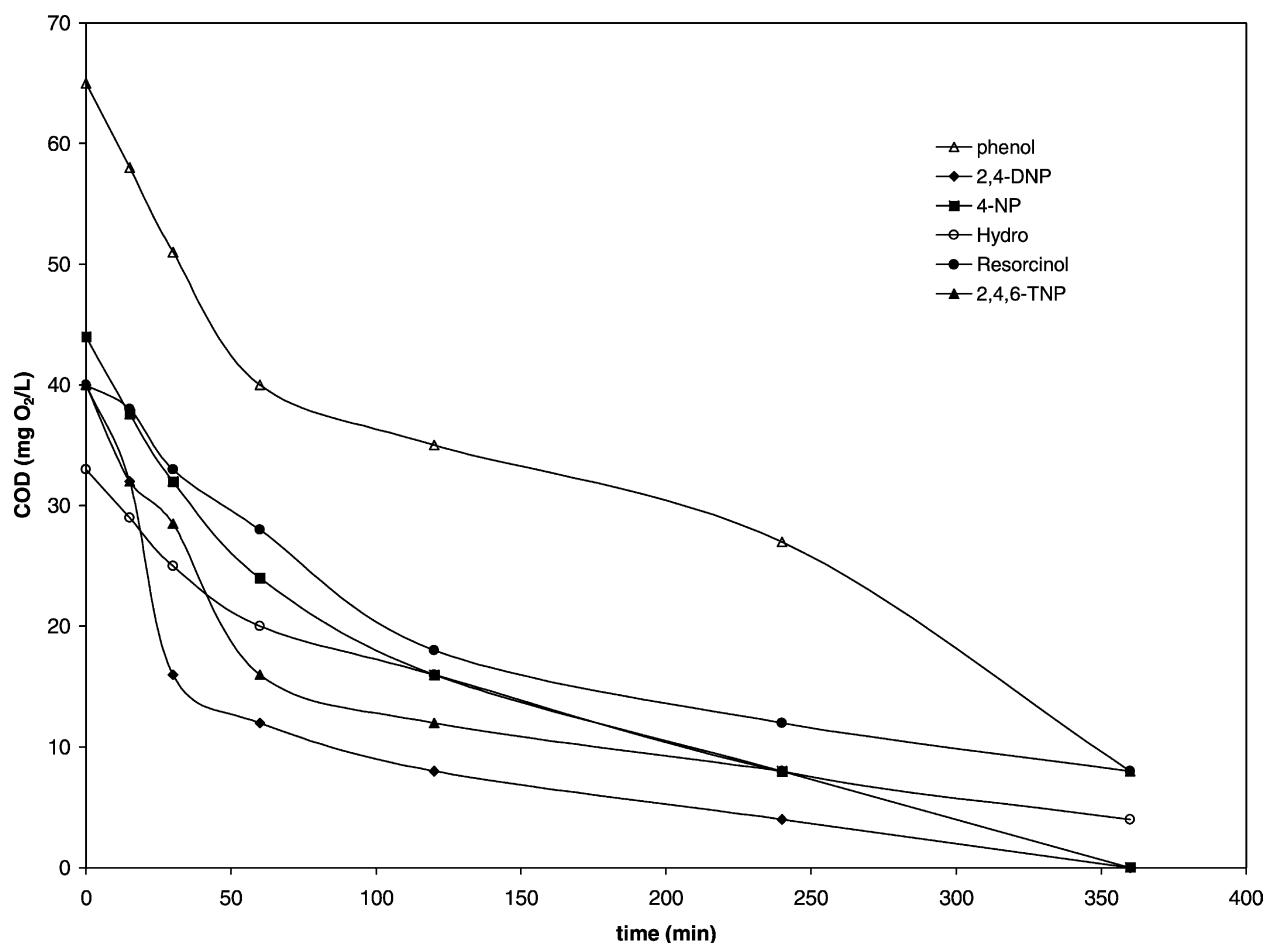
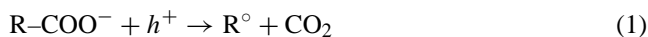


Fig. 5. Kinetics of COD disappearance. Conditions: $C_0 = 175 \mu\text{mol l}^{-1}$; $m(\text{TiO}_2) = 1 \text{ g}$; $V = 1000 \text{ ml}$; $T = 30^\circ\text{C}$; natural pHs.

y-axis are in agreement with the chemical formulae and with the stoichiometric coefficients expressed in Table 3.

The kinetic isotherms have a sigma shape indicating that they are in relation with the formation of the end products. The inflection point corresponds to a reaction time of ca. 30 min, it is equal to the opening of aromatic ring with the transient formation of carboxylic acids followed by the evolution of CO_2 according to the “photo-Kolbe” reaction (Eq. (1)):



3.3.2. Influence of pH on COD removal

Since substituted phenols to degrade can be at different pHs in industrial wastewater, experiments were performed

Table 3

Stoichiometric equations of the phenols total oxidation

4-NP	$\text{C}_6\text{H}_5\text{O}_3\text{N} + 7\text{O}_2 \rightarrow 6\text{CO}_2 + 2\text{H}_2\text{O} + \text{NO}_3^- + \text{H}^+$
2,4-DNP	$\text{C}_6\text{H}_4\text{O}_5\text{N}_2 + 7\text{O}_2 \rightarrow 6\text{CO}_2 + \text{H}_2\text{O} + 2\text{NO}_3^- + 2\text{H}^+$
2,4,6-TNP	$\text{C}_6\text{H}_3\text{O}_7\text{N}_3 + 7\text{O}_2 \rightarrow 6\text{CO}_2 + 3\text{NO}_3^- + 3\text{H}^+$
Resorcinol	$\text{C}_6\text{H}_6\text{O}_2 + 13/2\text{O}_2 \rightarrow 6\text{CO}_2 + 3\text{H}_2\text{O}$
Hydroquinone	$\text{C}_6\text{H}_6\text{O}_2 + 13/2\text{O}_2 \rightarrow 6\text{CO}_2 + 3\text{H}_2\text{O}$
Phenol	$\text{C}_6\text{H}_6\text{O} + 7\text{O}_2 \rightarrow 6\text{CO}_2 + 3\text{H}_2\text{O}$

at pH values: 2 and 10. By comparison with experiments performed at natural pH, we observe a considerably influence of pH upon the kinetics of COD disappearance. The results are represented under the form of linear transforms $\log(k_{\text{app}}) = f(\log[\text{H}^+]) = f(-\text{pH})$ (Fig. 6). This representation enables us to determine the kinetic partial order with respect to proton concentration by measuring the slopes of the curves. Despite of the dilated scale of the y-axis, the slopes actually have tiny values less than 0.1 in absolute value. This clearly indicates that protons do not intervene in the rate-limiting step of the photocatalytic system, in agreement with other results on pollutant removal [12]. Although the partial kinetic orders with respect to $[\text{H}^+]$ are small, we can observe two types of behavior. Nitrophenols are more degraded at lower pH compared to hydroxyphenols. At lower pH, the degradation rate of nitrophenolic compounds increases with an increasing number of nitro groups. This will be related to the acidity of these compounds. In fact at natural pHs, nitrophenols are totally ionized in water whereas hydroxyphenols are still in neutral forms. We believe that formed anions when the pH is lower than pH_{pzc} of TiO_2 ($\text{pH}_{\text{pzc}} = 6.5$), is responsible for the positive effect of pH on the kinetic orders with respect to $[\text{H}^+]$.

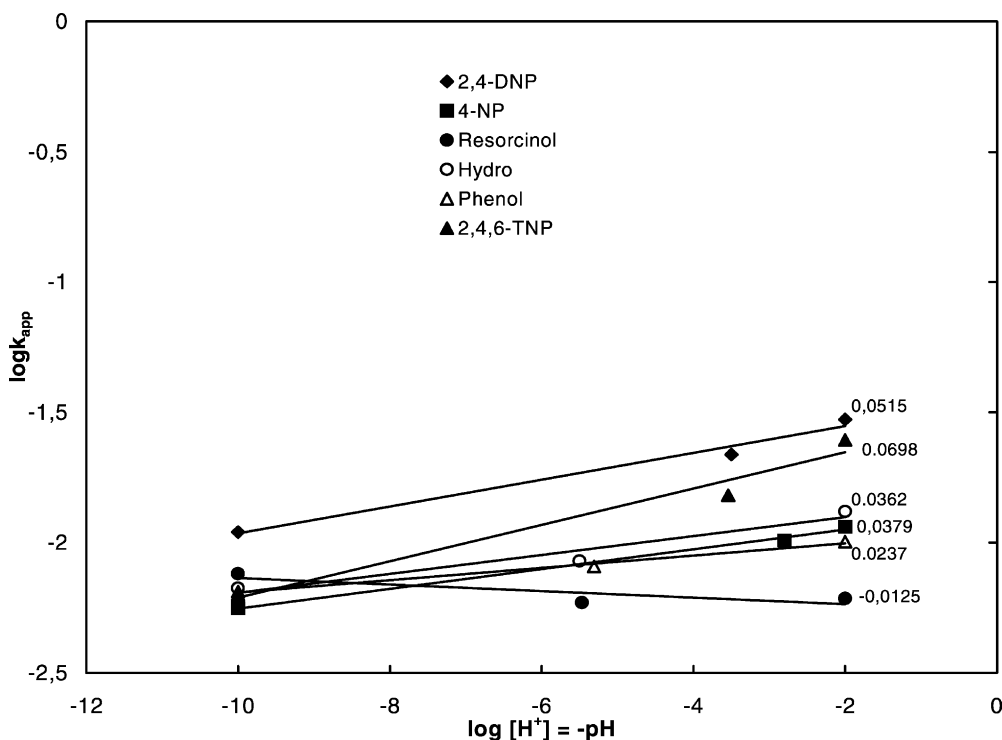


Fig. 6. Effect of pH on the kinetics of COD disappearance: the log–log plot of $k_{app} = f[H^+]$. Conditions: $C_0 = 175 \mu\text{mol l}^{-1}$; $m(\text{TiO}_2) = 1 \text{ g}$; $V = 1000 \text{ ml}$; $T = 30^\circ\text{C}$.

3.3.3. Evolution of nitrogen-containing final product

Photocatalytic degradation of nitrogen containing compounds generates NO_3^- , NO_2^- , NH_4^+ , N_2O and N_2 [13–16], according to the chemical structure surrounding nitrogen atom and experimental condition. The kinetics of NO_3^- , NO_2^- , NH_4^+ are given in Fig. 7 for 4-NP, 2,4-DNP and 2,4,6-TNP, respectively. For 4-NP, the nitrogen mass balance, obtained by adding all ions concentrations, almost corresponds to the final expected stoichiometric value. The others nitrophenols do not provide any nitrogen mass balance in the aqueous phase. It is noted that the formation rate of NO_3^- from 2,4,6-TNP (picric acid) is relatively slow when it is taken into consideration that picric acid possesses three nitro groups. This phenomenon was observed by Tanaka et al. [17]. By comparing the initial rates, nitrite appears as a primary product. The nitro group in nitrophenols is converted first in nitrite ions then oxidized quickly in nitrates. Similar observations have been reported by Maurino et al. [18] in photocatalytic degradation of various mononitrophenols.

The formation of ammonium has been explained by a sequence of reductive steps of nitro groups, as observed in the photocatalysed reductive transformation of nitrobenzene [19]. Other authors [20] had reported that nitrite ions could be reduced directly on semiconductor surface to give ammonia. These observations imply that some part of nitro group subsists after the opening of aromatic ring [21,22] and NH_4^+ is formed from aliphatic nitrogen-containing intermediates generated by the ring opening.

3.4. Relationships between COD removal and biodegradability

The knowledge of the relationship between the structure and biodegradability of the organic compounds makes possible the evaluation of the biological treatment of wastewater and the removal of the organic compounds by the treatment process. For the substituted aromatic compounds, good correlation between the biodegradability and the electronic effects (expressed by the constant of Hammett) of the substituent were recorded [23]. These correlations makes possible the prediction of biodegradation rates of organic compounds in the environment, and facilitate the comprehension of the biological degradation mechanism.

The nature, number, and position of the substituents on the aromatic ring influence the biodegradability of aromatic compounds. To try to clarify this aspect, the biodegradability of substituted phenols with NO_2 , and OH at *ortho*-, *meta*- and *para*-positions was tested. The ratio of BOD to COD, representative of the solution biocompatibility, is summarized in Table 4. The BOD values are obtained after 5 days incubation period, i.e. BOD_5 . It should be noticed that BOD_5/COD ratios higher than 0.4 indicate a readily and rapidly degradable solution, while ratios below 0.4 involve the presence of slowly degradable compounds.

The results presented in Table 4, agree with those recorded in literature [23]. For the same position, the presence of OH group facilitates the biological degradation while nitro group decreases it. Generally, the group that increases the

biological degradation includes mainly the substituents, which can increase the density of electron of the aromatic ring while the group that lowers the biological degradation includes the substituents that decrease the density of electron. These substituents activate or deactivate the aromatic ring with respect to the electrophile attack by oxygen. In the case of 4-nitrophenol, we recorded a strong increase in the DBO₅/DCO ratio after 6 h of exposure to UV. This ratio reaches the value of 1.29. We can explain this increase by the disappearance of NO₂ groups and the hydroxylation of the aromatic ring returning thus to more degradable formed intermediary. We also notice that the higher number of NO₂

Table 4
Biodegradability of different substituted phenols

Phenolic compound	DBO ₅ /DCO	
	Initial solutions	After photo-treatment (2 h)
Phenol	0	0.15
Hydroquinone	0.31	0.645
Resorcinol	0	0.224
4-NP	0.108	0.6
2,4-DNP	0.05	0.56 ^a
2,4,6-TNP	0.08	0.43

^a For the 2,6-dinitrophenol DBO₅/DCO ratio is determined after only 1 h of UV exposure.

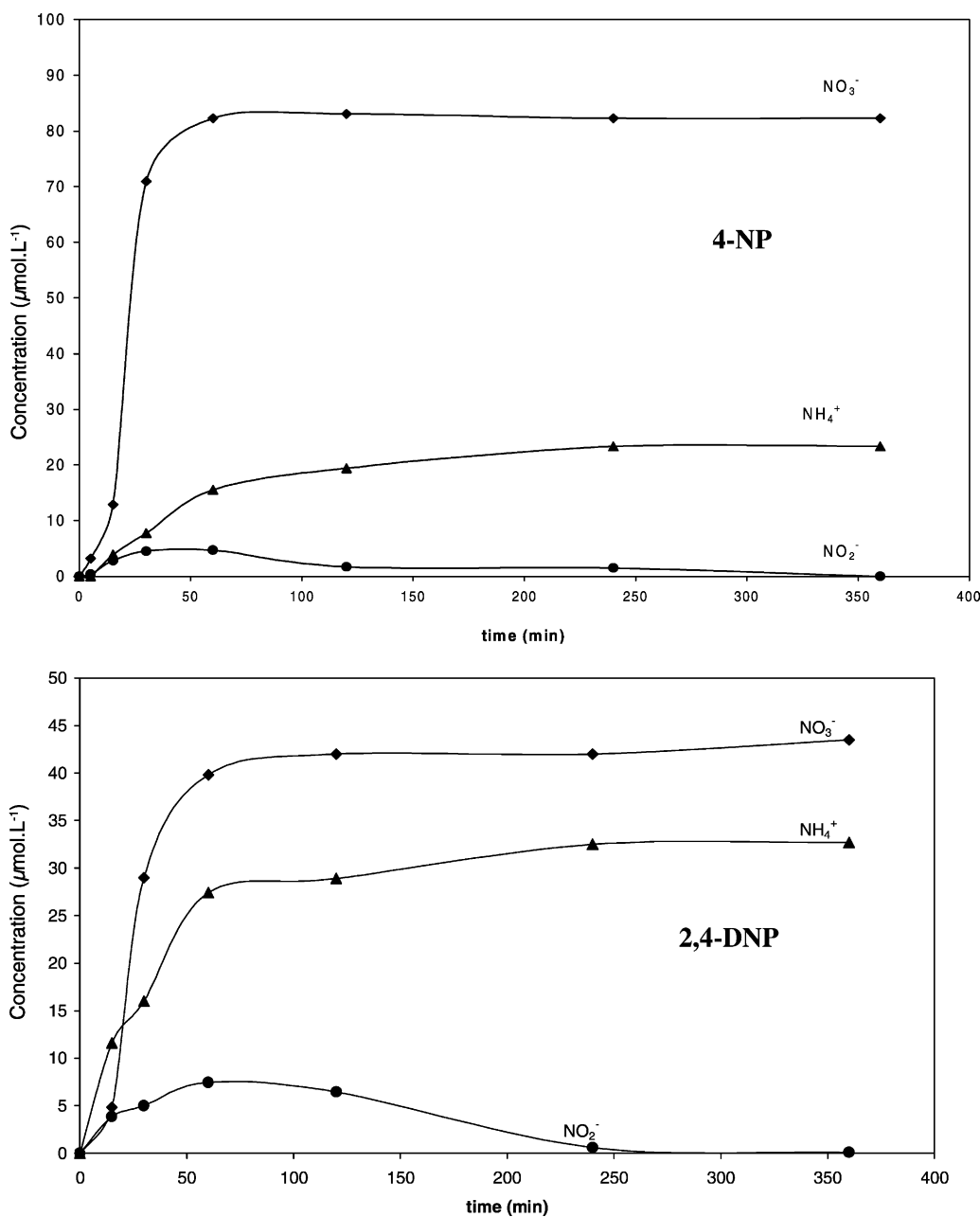


Fig. 7. Time evolution of nitrate, nitrite and ammonium ions in the degradation of 4-NP (top), 2,4-DNP (middle) and 2,4,6-TNP (bottom). Conditions: $C_0 = 175 \mu\text{mol.l}^{-1}$; $m(\text{TiO}_2) = 1 \text{ g}$; $V = 1000 \text{ ml}$; $T = 30^\circ\text{C}$; natural pHs.

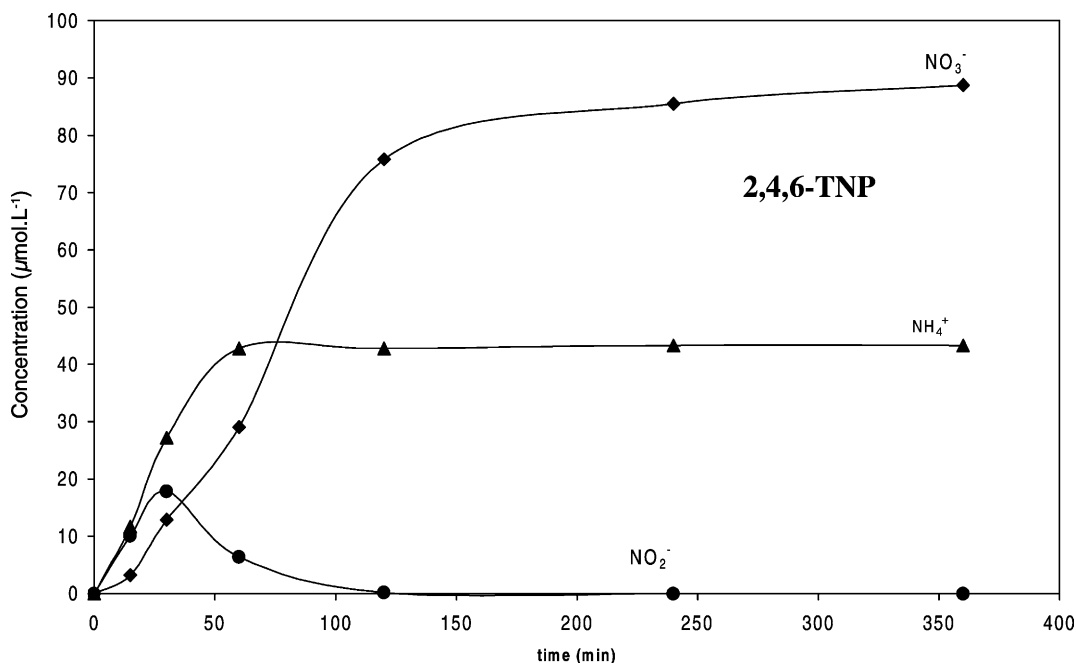


Fig. 7. (Continued).

groups decreases ratio DBO₅/DCO. Indeed the aromatic ring is deactivating considerably which decreases the biodegradation of these phenolic compounds. It is not observed a direct correlation between the structure of the substituted phenolic compound and the biodegradation of its photo-treated solution. However, all the photo-treated solutions which we evaluated the ratios BOD₅/COD show values higher than those recorded in initial solutions which is an indication of the positive effect of the applied photo-treatment.

4. Conclusion

Direct UV-irradiation of TiO₂ catalyst suspended in aqueous solutions is able to destroy some hydroxyphenol (hydroquinone and resorcinol) and nitrophenols (4-nitrophenol, 2,4-dinitrophenol and 2,4,6-trinitrophenol). The photodegradation of these phenolic compounds follows pseudo-first-order kinetics. Their photoreactivity are affected in various manners by both electronic character (electro-withdrawing or electro-donor) and by the position of the substituent groups in the aromatic ring. The Hammett constant, whose value translates the electronic effect of the different substituents on the aromatic ring for studied phenols proved to be the most adequate describer of the susceptibility of a substance to be degraded by photocatalysis.

The initial pH of irradiated solution is an important variable to take into account in the photodegradation of these phenolic compounds. It was found that the deterioration of nitrophenols (COD removal) could be accelerated in acidic medium whereas hydroxyphenols are less sensitive to pH variations. Photocatalysis convert nitro groups in nitrophenols

to NO₃⁻ through the intermediate formation of NO₂⁻ ions. The NH₄⁺ ions were obtained from aliphatic nitrogen containing intermediates generated by the ring opening.

It was also found that the DBO₅ in the phenolic solutions increased with the COD decreased during the photodegradation reaction. It indicated that reaction in the photoreactor might break down specific molecular bonds or rearrange molecular structures of some organic complexes to simpler compounds, in which some non-biodegradable organic substances were converted to biodegradable forms.

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