

Research Article

Photocatalytic Degradation of Polynitrophenols on Various Commercial Suspended or Deposited Titania Catalysts Using Artificial and Solar Light

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Phenol (PH) and three polynitrophenols (4-nitrophenol (PNP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP)) were photocatalytically degraded by using titania under either artificial or solar light. These four reactions were chosen as test reactions to compare the efficiencies of two suspended commercial titania photocatalysts (Degussa P-25 and Millennium PC-500). It appears that P-25 has a higher initial efficiency in all nitrophenol disappearance reactions. However, for the overall degradation rate, measured by the chemical oxygen demand (COD) disappearance, the performance of PC-500 was similar to that of P25. This was attributed to a favorable textural effect since PC-500 has a much higher surface area which facilitates the readsorption of intermediates. PC-500 was subsequently supported on a special photoinert paper provided by Ahlstrom Company (38-Pont Evêque, France). The influence of the silica binder used for sticking titania particles on the paper fibers was put in evidence as an inhibitor of the coulombic adsorption of anionic species, especially 2,4,6-trinitrophenol, because of the low pzc of silica. Once validated, this supported photocatalyst was introduced in an autonomous solar pilot photoreactor identical to the several prototypes built in the European AQUACAT program. It was demonstrated that the purification of water could be efficiently obtained in a larger scale without any final tedious filtration.

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1. INTRODUCTION

The photocatalytic degradation of toxic compounds in aqueous medium provides a new opportunity for the treatment of urban and agricultural wastewater. Nitrophenols, for example, are released into the environment because of their wide use in syntheses of dyes, pesticides, plasticizers, and solvents. In addition, they are formed as degradation products of many chemicals such as herbicides (see for instance herbicides nitrofen [1] and parathion [2]) when they are exposed to sunlight [3]. The photocatalytic degradation rate of the different nitrophenols depends on various parameters, such as temperature [4], pH [4, 5], initial concentration of the pollutant [4–6], and light intensity. Various studies have shown that the number and positions of substituent in some aro-

matic compounds are widely linked to their photocatalytic reactivity [7–11].

Advanced oxidation processes (AOPs) have been proposed as an alternative for the treatment of wastewater containing nitrophenols. A lot of studies focused on these processes [12–16] have pointed out that, although the reacting systems were different [17, 18], they are all characterized by the same chemical feature, that is, the production of OH^\bullet radicals, which as the second best oxidant after fluorine, is the active species responsible for the destruction of organic pollutants [19, 20].

The objective of this study was the validation of the performances of two commercial catalysts using the photocatalytic degradation of polynitrophenols, (4-nitrophenol (PNP), 2,4-dinitrophenol (DNP), and 2,4,6-trinitrophenol

TABLE 1: Physicochemical characteristics of polynitrophenols.

Compound	Mw (g/mol)	λ_{\max} (nm)	ϵ (L · mg ⁻¹ · cm ⁻¹)	pKa	pH
Phenol	94.11	270	0.0153	9.20	6.7
4-nitrophenol (PNP)	139.11	317	0.0623	7.16	5.8
2,4-dinitrophenol (DNP)	184.11	260	0.0560	4.00	5.3
2,4,6-trinitrophenol (TNP)	229.11	356	0.0461	0.80	4.0

TABLE 2: Langmuir parameters of phenolic compound adsorption.

Reactants	Degussa P25			PC500			PC500/Paper 1048	
	q_{\max} (mg/g)	K_{ads} (L/mg)	n_{ads} (mol/nm ²)	q_{\max} (mg/g)	K_{ads} (L/mg)	n_{ads} (mol/nm ²)	q_{\max} (mg/g)	K_{ads} (L/mg)
Phenol	4.87	0.031	0.62	6.27	0.136	0.125	10.44	0.290
4-nitrophenol (PNP)	10.25	0.046	0.88	9.11	0.290	0.120	8.32	0.217
2,4-dinitrophenol (DNP)	15.52	0.025	1.00	11.73	0.110	0.120	6.60	2.780
2,4,6-trinitrophenol (TNP)	18.93	0.020	1.00	15.86	0.021	0.130	5.66	7.00

n_{ads} : area density of adsorbed phenol molecules (in molecules/nm²).

(TNP) or picric acid (TNP)) as test reactions. Such degradations are now well known [4–6, 17, 18, 21]. These reactions were performed in presence of powder or of supported TiO₂. In the last case, we used Millennium PC500 titania coated on an Ahlstrom nonwoven paper to validate its performances. Subsequently, this deposited photocatalyst was used in an “AQUACAT” pilot solar photoreactor to clean and reuse contaminated water in semiarid areas. This is in line with the pioneer works performed at Plataforma Solar de Almeria (PSA) on many pollutants [22–25].

2. EXPERIMENTAL

2.1. Materials and reagents

Titanium dioxide Degussa P-25 was used as the reference photocatalyst. It is constituted of 80% anatase and 20% rutile and its BET surface area is 50 m²/g, corresponding to a mean particle size of *ca.* 30 nm. Millennium PC500 titanium dioxide (100% anatase, specific surface area of 320 m²/g) was also used either as a powder in slurry or supported on a nonwoven paper (paper Ahlstrom 1048), offered by Mr. J. Dussaud from Ahlstrom Company. The area loading in TiO₂ was 18 g/m². Supported titania has been tested by using either UV artificial light in laboratory experiments or solar light for outside experiments in South Tunisia. The phenolic compounds were purchased from Aldrich (38-Ville D’Abeau, France) and used as received without further purification. Their solutions were prepared using twice-distilled water. Their physicochemical characteristics are given in Table 1.

2.2. Apparatus

A one-liter reactor was used in the laboratory experiments. It is equipped with a plunging tube in which a Philips HPK 125 W UV-lamp was placed vertically. To avoid the heating of the solution, water was circulated through a cylindrical jacket, made of Pyrex and located around the plunging tube.



FIGURE 1: Photograph of the autonomous AQUACAT solar pilot prototype.

The photon flux of the UV irradiation reaching the exposed inner part of the reactor at $\lambda > 290$ nm was measured to be around $6 \cdot 10^{-6}$ Einstein (mol of photons) per second. Another photoreactor was employed for solar experiments. It is an autonomous pilot scale prototype developed by the European Research Project AQUACAT using TiO₂ supported on Ahlstrom paper 1048 (Figure 1). This new photoreactor was employed for solar experiments and consists of one sun collector, one water tank, and one electrical circulating pump connected with a photovoltaic panel. The reactor itself consists of glass tubes connected in series and placed on a fixed platform inclined at a 37° angle corresponding to the local latitude for collecting a maximum solar irradiation around noon. The water circulating flow was fixed at 12 L/min. The total volume (V_T) of the water treated was 20 L and divided in 12 L in the irradiated glass tubes and 8 L in the tank. This pilot plant is a plug-flow reactor connected to a tank with recirculation. This ensemble corresponds to a batch reactor. During experiments, the temperature of the effluent varied in the range of 35–40°C, that is, close to the optimum for photocatalysis [19, 20].

TABLE 3: Kinetic data of the photocatalytic degradation of nitrophenols.

	P25			PC500			Paper 1048		
	$K_{app} \cdot 10^2$ (mn^{-1})	$K_{app}/g \cdot 10^2$ ($\text{mn}^{-1} \cdot \text{g}^{-1}$)	ro (ppm/min)	$K_{app} \cdot 10^2$ (mn^{-1})	$K_{app}/g \cdot 10^2$ ($\text{mn}^{-1} \cdot \text{g}^{-1}$)	ro (ppm/min)	$K_{app} \cdot 10^2$ (mn^{-1})	$K_{app} \cdot 10^2$ ($\text{mn}^{-1} \cdot \text{g}^{-1}$)	ro (ppm/min)
PH	0.56	1.12	0.093	0.53	1.06	0.13	0.92	1.08	0.11
PNP	1.00	2.00	0.184	0.73	1.46	0.16	0.67	0.78	0.10
DNP	1.18	2.36	0.240	0.96	1.92	0.18	0.48	0.56	0.06
TNP	1.98	3.96	0.298	1.28	2.56	0.24	0.33	0.38	0.05

TABLE 4: Initial COD values in mgO_2/L for nitrophenols having the same initial ponderal concentration (30 mg/L). Apparent first-order rate constant K_{app} and corresponding specific one K_{app}/g_{cat} .

	COD initial (mg/L)	P25		PC500		Paper 1048	
		K_{app} (mn^{-1})	K_{app}/g ($\text{mn}^{-1} \cdot \text{g}^{-1}$)	K_{app} (mn^{-1})	K_{app}/g ($\text{mn}^{-1} \cdot \text{g}^{-1}$)	K_{app} (mn^{-1})	K_{app}/g ($\text{mn}^{-1} \cdot \text{g}^{-1}$)
Phenol (PH)	74	0.50	1.0	1.15	2.30	0.80	0.94
4-nitrophenol (PNP)	50	0.80	1.6	1.73	3.46	1.12	1.31
2,4-dinitrophenol (DNP)	45	1.28	2.5	2.19	4.38	1.66	1.95
2,4,6-trinitrophenol (TNP)	30	1.84	3.7	3.14	6.28	3.62	4.25

TABLE 5: Solar degradation and mineralization kinetics (K_{app} , r_0) of phenolic compounds.

	$K_{app} \cdot 10^2$ (mn^{-1})		r_0 (mol/L · min)	
	Degradation	Mineralization	Degradation	Mineralization
Phenol	0.17	0.15	0.068	0.066
4-nitrophenol (PNP)	0.42	0.23	0.105	0.083
2,4-dinitrophenol (DNP)	0.28	0.45	0.080	0.108
2,4,6-trinitrophenol (TNP)	0.13	0.67	0.055	0.150

2.3. Procedure

2.3.1. Laboratory experiments

One liter of aqueous solution of each phenolic compound ($C_0 = 30 \text{ mg/L}$) was introduced into the lab reactor and an amount of 500 mg of TiO_2 (P25 or PC500) was added to get a final concentration of 0.5 g/L. The same photoreactor was used with PC500- TiO_2 photocatalyst supported on Ahlstrom paper 1048. A sheet of this titania supporting paper was deposited on a glass cylinder of 12.5 cm in diameter and 12 cm high. The corresponding concentration of TiO_2 was about 850 mg/L . The degradation reactions were carried out at 293 K and at natural pH values (6.7, 5.8, 5.3, and 4.0, for phenol, PNP, DNP, and TNP, resp.). The suspension was first stirred in the dark for 90 minutes before irradiation in order to reach the adsorption equilibrium before starting the photocatalytic reaction.

2.3.2. Solar experiments

The total volume (V_T) treated was 20 L and the water flow rate was fixed at 12 L/min. The suspension was first stirred in the dark for 90 minutes before irradiation to reach equilibrated adsorption. Stirring was obtained by recirculating the total volume of 20 L at a flow rate of 12 L/min obtained by

the electrical pump run by the photovoltaic panel. As for laboratory experiments, the initial concentration of phenols was fixed at 30 mg/L .

2.4. Analyses

Before analysis, the aqueous samples were filtered through a $0.45 \mu\text{m}$ membrane filter to remove TiO_2 agglomerates in suspension. A Shimadzu-1700 UV-vis spectrophotometer was used to determine the concentration of the nitrophenols and to follow their kinetic disappearance. Calibration plots based on Beer-Lambert's law were established to relate the absorbance to the concentration. The molar extinction coefficients for phenol, 4-nitrophenol (PNP), 2,4-dinitrophenol (DNP), and 2,4,6-trinitrophenol (TNP) were estimated at 270, 317, 260, and 356 nm, respectively. Chemical oxygen demand (COD) was measured using the acidic dichromate method with a bioblock COD analyzer.

3. RESULTS AND DISCUSSION

3.1. Adsorption of phenolic compounds on titania

The adsorption of the different phenolic compounds is studied at room temperature ($20 \pm 2^\circ\text{C}$) and at natural pH. The

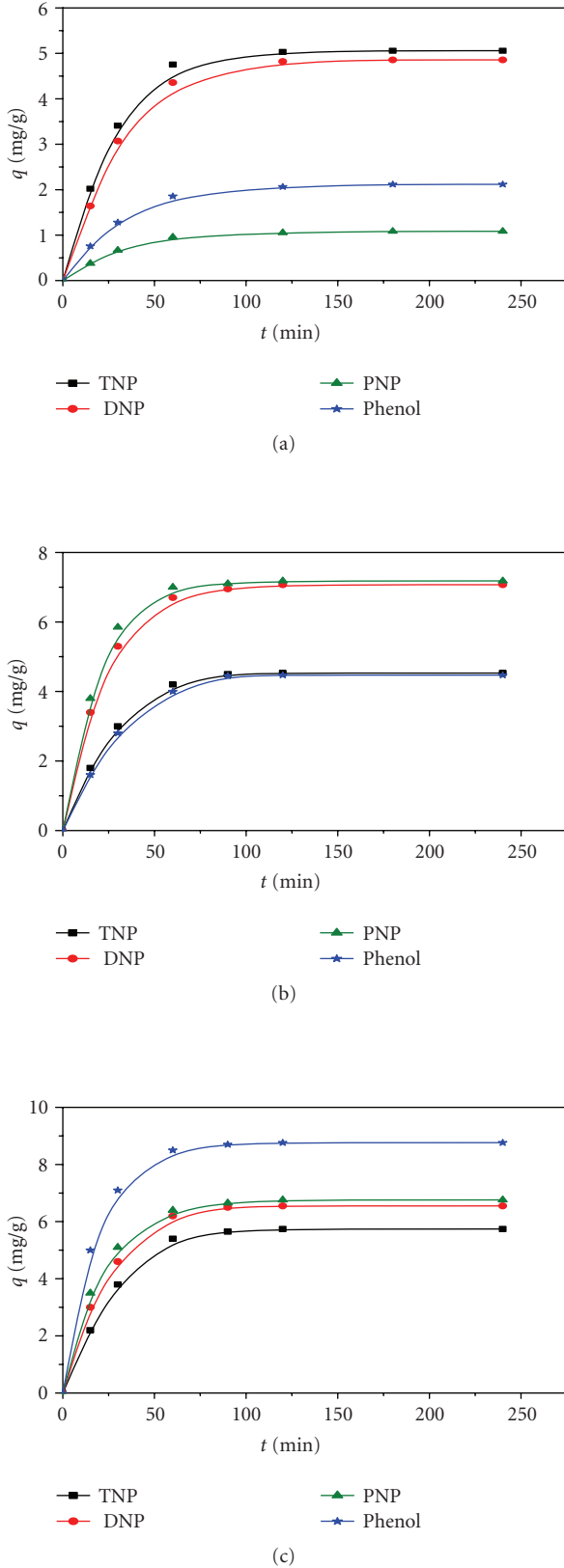


FIGURE 2: Kinetics of adsorption of phenolic compounds in presence of different catalysts (a). Degussa P25, (b) Millennium PC-500, and (c) Millennium PC-500 TiO₂ deposited on Ahlstrom paper 1048. Experimental conditions: $C_0 = 30$ mg/L, $[P25] = [PC500] = 2.5$ g/L, $V = 100$ mL, natural pH.

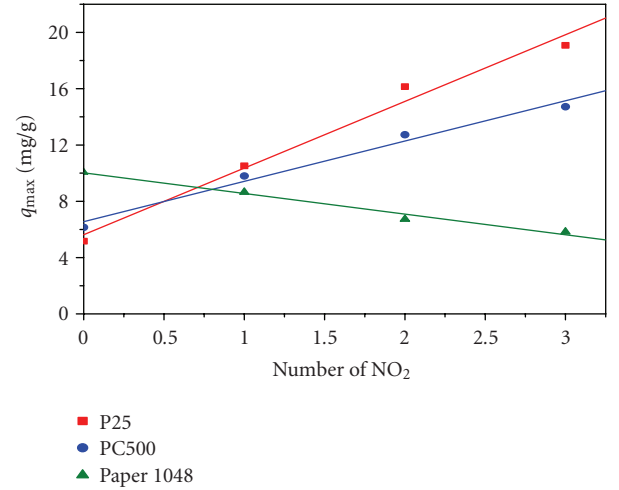


FIGURE 3: Linear variations between the maximum quantity of adsorbed polynitrophenols q_{max} and the number of NO₂ substituent.

adsorption kinetic curves for the four phenolic compounds (phenol, PNP, DNP, and TNP) on different catalysts are represented in Figure 2. The initial concentration is fixed at 30 mg/L. For each phenolic compound, whatever the catalyst employed, the steady state of adsorption is reached within 90 minutes. Therefore, this time has been selected as the duration of the dark period previously to irradiation. The degradation initiates at the equilibrium of adsorption. The maximum absorbed quantities q_{max} and the adsorption constants K_{ads} of phenols were determined at different initial concentrations varying between 5 and 30 mg/L using the linear transform of the Langmuir equation,

$$\frac{C_e}{q_e} = \frac{1}{K q_{max}} + \frac{C_e}{q_{max}}, \quad (1)$$

where C_e is the equilibrium concentration of the phenolic compounds and q_e is the quantity of the adsorbed phenolic compounds at TiO₂ surface. The linearity of the curves clearly indicates that the Langmuir isotherm is correctly observed, implying a monolayer adsorption model. The calculated values are listed in Table 2.

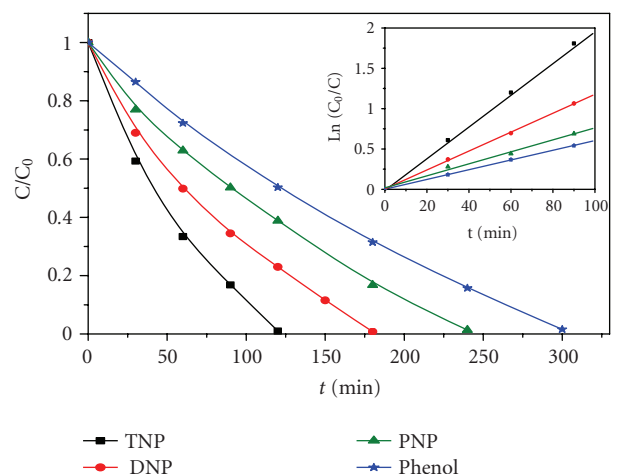
The following general observations can be made. For both unsupported Degussa P25 and Millennium PC-500 photocatalysts, the maximum quantities of adsorbed phenolic compounds increase in the following order:

$$\text{Phenol} < \text{PNP} < \text{DNP} < \text{TNP}. \quad (2)$$

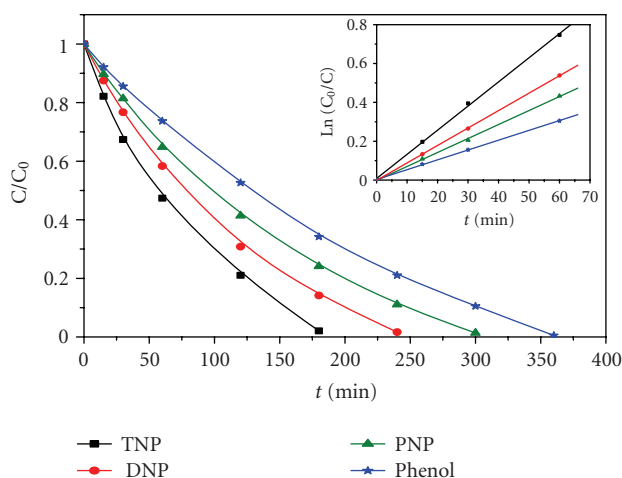
This is in line with an ionic type of adsorption. Because of their decreasing pKa's and of the resulting pH's of the solutions, the surface of titania samples gets positively charged according to



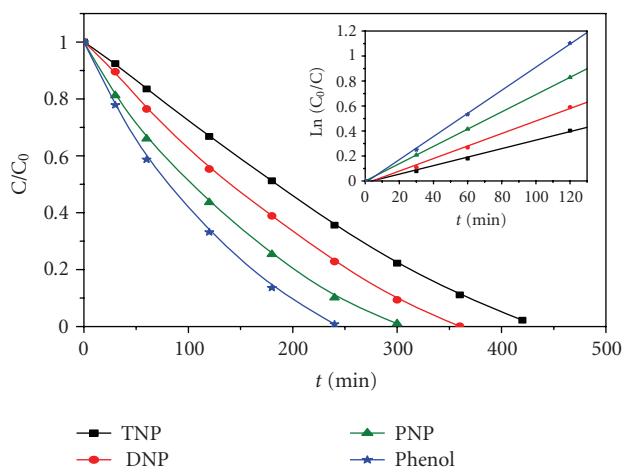
This favors the coulombic attraction and the related adsorbed quantities of the nitrophenols.



(a)



(b)



(c)

FIGURE 4: Kinetics of the photocatalytic degradation of phenols in presence of different catalysis ((a) P25, (b) PC500, and (c) supported TiO_2 (paper 1048)). In the insert, first-order linear transforms $\text{Ln } C_0/C = f(t)$. Experimental conditions: $C_0 = 30 \text{ mg/L}$, $[\text{P25}] = [\text{PC500}] = 0.5 \text{ g/L}$, $V = 1 \text{ L}$, natural pH.

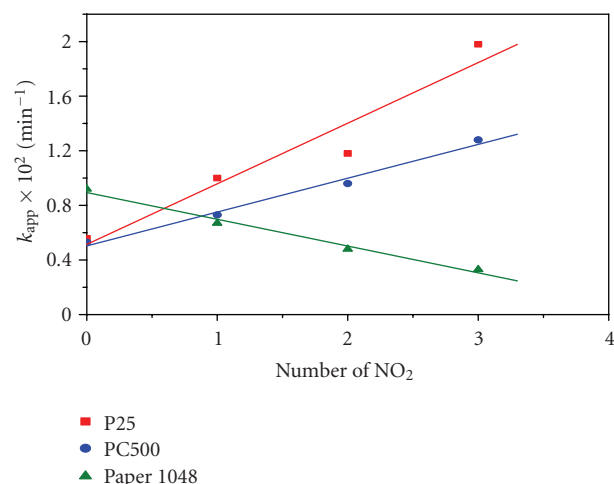


FIGURE 5: Linear variations of the rate constants with the number of NO_2 substituents.

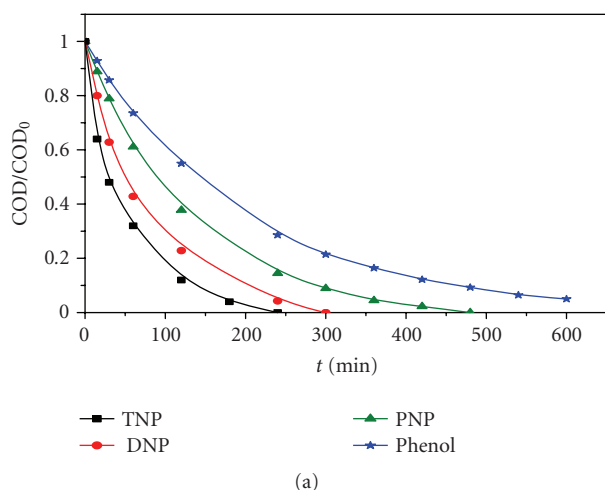
By contrast, the variations of q_{max} are opposite for PC-500/paper 1048. This is due to the presence of the amorphous silica binder. Since the pzc of silica is very low in comparison with that of titania (56), there is a coulombic repulsion of the anionic polynitrophenols by the negatively charged together (silica binder + titania catalyst). Surprisingly, there is a proportional variation between q_{max} and the number n of nitrosubstituents as illustrated in Figure 3.

3.2. Photocatalytic degradation of the polynitrophenols

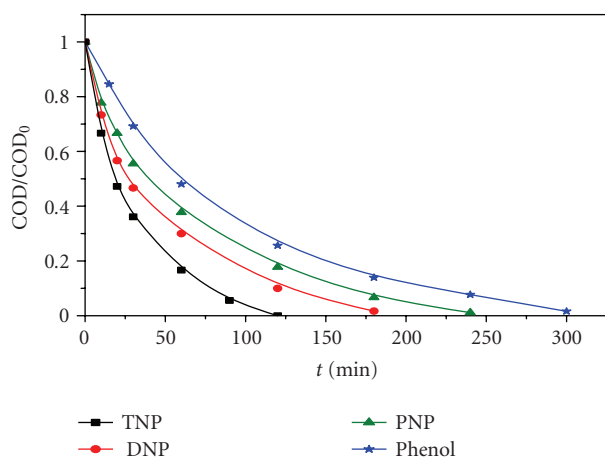
The disappearance rates of nitrophenolic compounds in contact with the three UV-irradiated photocatalysts are given in Figure 4. Starting with an initial concentration of 30 mg/L , the total disappearance of all nitrophenolic compounds is reached in between 2 and 7 hours.

All reactions followed an apparent first-order verified by the linear transforms $\text{Ln}(C_0/C) = f(t)$ illustrated in the insert in Figure 5. The slopes give the apparent rate constants listed in Table 3. The initial rates of disappearance in ppm/min are in the following order: $\text{TNP} > \text{DNP} > \text{PNP} > \text{phenol}$. It appears that PC500 is less efficient for the photocatalytic disappearance of nitrophenols than P25. This is also observed for specific activities, that is, rates per g of catalyst (see Table 3). For PC500 supported on Ahlstrom paper 1048, the order is different—phenol < PNP < DNP < TNP.

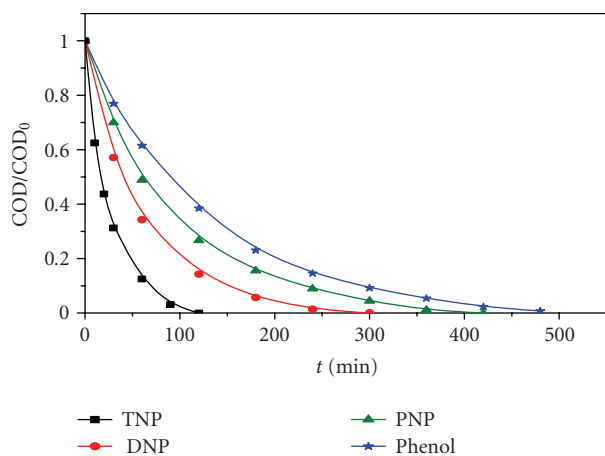
All these differences can be explained by considerations about adsorption. The rates of polynitrophenol disappearance vary in parallel with the quantities of adsorbed pollutants as indicated by the corresponding parameters indicated in Tables 2 and 3. In addition, this is confirmed by the parallel proportional variations of either the quantities of polynitrophenols adsorbed (Figure 3) or of the rate constants as function of the number of NO_2 groups (Figure 5). This confirms the Langmuir-Hinshelwood mechanism involved in these reactions.



(a)



(b)



(c)

FIGURE 6: Kinetics of COD disappearance of nitrophenols in presence of different catalysts ((a) Degussa P25, (b) Millennium PC-500, and (c) PC-500 supported on Ahlstrom paper 1048). Experimental conditions: $C_0 = 30$ mg/L, $[P25] = [PC500] = 0.5$ g/L, $V = 1$ L, natural pH.

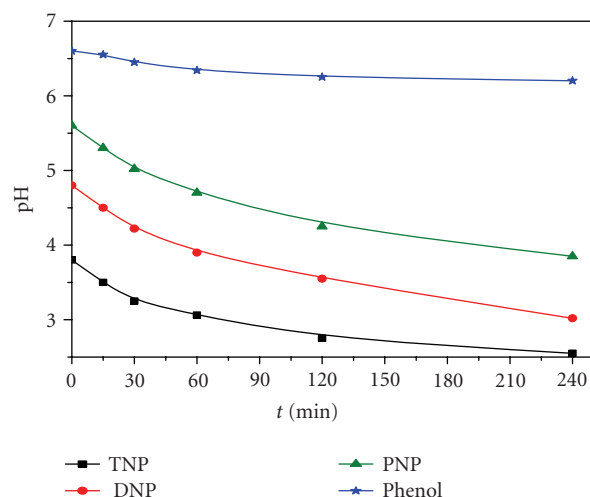


FIGURE 7: Kinetics of pH variations during the photocatalytic degradation of nitrophenols. Experimental conditions: $C_0 = 30$ mg/L, $[P25] = [PC500] = 0.5$ g/L, $V = 1$ L

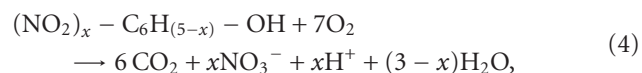
3.3. Kinetics of COD disappearance

The kinetics of the total mineralization of nitrophenols has been determined by following the disappearance of the chemical oxygen demand (COD). The kinetic isotherms are given in Figure 6. For all nitrophenols, COD reached 0 within 8 hours. The initial values of COD are in agreement with the chemical formulas and with the stoichiometries of all nitrophenols degradation reaction, TNP having the smallest COD.

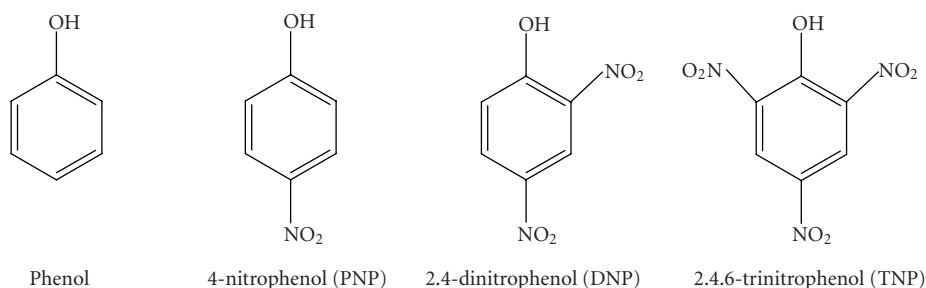
Although titania Degussa P-25 has the highest activity for nitrophenols disappearance, it clearly appears from Table 4 that PC-500 has an important efficiency in their total mineralization. This can be explained by a favorable textural effect. Since total degradation involves many consecutive reactions before reaching CO_2 , the readsorption of all the numerous intermediates is favored by catalyst having large surface areas, which is the case of PC-500. This advantage can be transposed to PC-500 supported on paper Ahlstrom 1048, as seen from data in Table 4. This underlines the interest of using supported catalyst to decontaminate wastewater by avoiding the tedious final filtration step, which strongly increases the overall cost of this potential treatment.

3.4. Kinetics of pH variations during the degradation of phenols

According to the stoichiometry of the total oxidation reaction,



the pH of the reaction medium is expected to decrease except for phenol ($x = 0$). This is actually observed with its temporal variations given in Figure 7. Therefore, the kinetics of pH variations is a good indicator of nitrophenols degradation or, at least, of their denitration. However, pH in the



SCHEME 1

UV-irradiated titania slurry is a rather important and complex parameter since it governs (i) water dissociation equilibrium, (ii) the surface charge of titania with respect to its pzc, and (iii) the ionization state of the organic reactants and of their intermediates. In addition, it also depends on the degradation of other pollutants present in the water to be treated. Nevertheless, in a batch photoreactor, its steady-state final value could be an easy and cheap indicator of the final reaching of total mineralization.

3.5. Solar experiments in the autonomous pilot plant

The polynitrophenol degradation reactions have been transposed to the solar pilot photoreactor and used to determine the efficiency of supported PC500 TiO₂ using solar energy in South Tunisia. This pilot plant is a plug-flow reactor connected to a tank with recirculation. This ensemble corresponds to a batch reactor. Because of the design of the reactor and of the varying solar radiant flux, a direct comparison with the results obtained in laboratory would not be correct. Only basic fundamental features are comparable for laboratory and pilot results. Actually, all reactions followed an apparent first-order kinetics, confirmed by the linear transforms $\ln C_0/C = f(t)$ in the inserts in Figure 8. The rate constants of the disappearance of nitrophenols are in a similar order of reactivity, PNP > DNP > phenol > TNP. The kinetic parameters of COD disappearance, which are illustrated by Figure 9 and listed in Table 5 show that TNP has the higher rate of COD disappearance as in laboratory experiments.

4. CONCLUSIONS

The photocatalytic degradation reactions of phenol and of mono-, di-, and trinitrophenol, chosen as test reactions to compare the efficiencies of two suspended commercial titania photocatalysts (Degussa P-25 and Millennium PC500), underlined the difficulty and complexity in objectively comparing two solids. If Degussa P-25 appeared easily as that having the higher initial efficiency in all nitrophenol disappearance reactions (as mostly observed in literature), however, for the overall degradation rate, measured by the chemical oxygen demand (COD) disappearance, the performances of PC-500 were similar to its own ones. This was attributed to

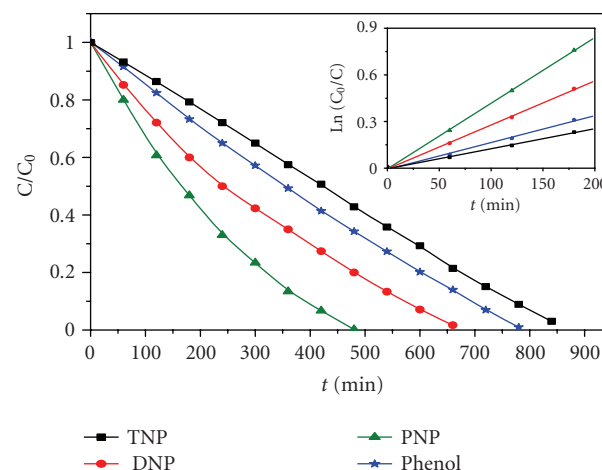


FIGURE 8: Experiments with pilot plant using solar energy, phenols disappearance. In the insert: first-order linear transforms $\ln C_0/C = f(t)$ of nitrophenols degradation. Experimental conditions: $C_0 = 30$ mg/L, $V = 20$ L, TiO₂ supported on Ahlstrom paper 1048, natural pH.

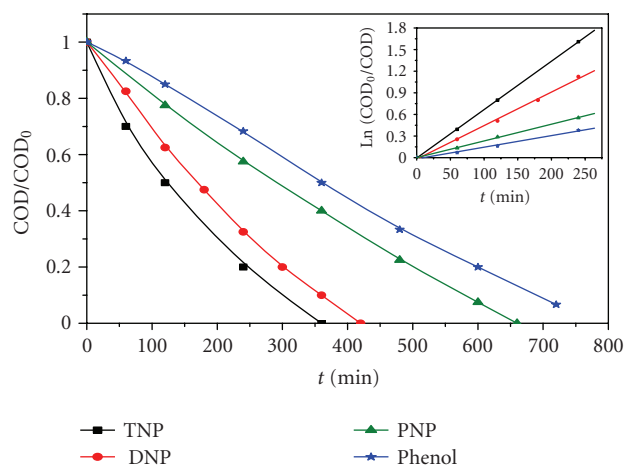


FIGURE 9: Experiments with pilot plant using solar energy, Kinetics of COD disappearance, in the insert: first-order linear transforms $\ln (COD_0)/COD = f(t)$ of nitrophenols mineralization. Experimental conditions: $C_0 = 30$ mg/L, $V = 20$ L, supported TiO₂ (paper 1048), natural pH.

a favorable textural effect since PC-500 has a much higher surface area, which facilitates the readsorption of the very large number of intermediates. When PC-500 was subsequently supported on a special photoinert paper provided by Ahlstrom Company, the presence of the silica binder, used for sticking titania particles on the paper fibers, perturbs several key parameters, principally the natural pH, because of the low pzc of silica. It acts as an inhibitor of the coulombic adsorption of anionic species, especially, 2,4,6-trinitrophenol. However, despite this negative influence, the supported photocatalyst when introduced in an autonomous AQUACAT solar pilot photoreactor clearly demonstrates that it can achieve purification of water with a reasonable efficiency, very compatible with the use of solar energy at a larger scale. In particular, it avoids the final tedious filtration necessary (i) to provide clean water and (ii) to recover and recycle the catalysts. Since filtration is declared as redhibitory by the chemical engineering point of view, this stresses the usefulness of such a material.

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