A COMPARISON OF SLURRY AND IMMOBILIZED TIO$_2$ IN THE PHOTOCATALYTIC DEGRADATION OF PHENOL

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Abstract— The photocatalytic degradation of phenol was studied using slurry and immobilized TiO$_2$ as catalysts in order to compare the specific reaction rate constants, k_s and k_p. Losses from phenol evaporation, the time necessary to reach adsorption equilibrium, irradiation effects and photolysis rates were quantified. k_s was determined under rate-optimizing operating conditions, and k_p was determined using the amount of immobilized catalyst mass that gave the maximum pollutant degradation rates. k_s was two times larger than k_p when the calculations were made on catalyst mass basis. Experiments performed to study catalyst deactivation showed that k_p was approximately one-half of its initial value after 18 hours of phenol photodegradation. Also, among the photocatalytic degradation reactions of rhodamine B, tetracycline and phenol, the ratio of k_s to k_p was between 2.1 and 5.3 when the calculations were made on catalyst mass basis.

Keywords— Phenol; Rhodamine B; Tetracycline; Photocatalysis; TiO$_2$

I. INTRODUCTION

Many studies of the photodegredation of phenol catalyzed by TiO$_2$ illuminated with UV and near-UV light have been reported, and the phenol degradation pathways in the UV/TiO$_2$ system are well documented (de Lasa *et al*., 2005; Gorska *et al*., 2009). The data in Table 1 indicate pseudo-first order kinetics for phenol photodegradation in slurry reactors. Even in studies employing identical catalysts and initial phenol concentrations, the reported pseudo-first order specific reaction rate constants differ significantly, limiting the usefulness of the data.

The studies presented in Table 1 were conducted in slurry reactors. When slurry reactors are operated as photocatalytic reactors, the catalysts must be kept separate from the degraded products; this requirement leads to significant additional costs in reactor operation. However, the use of immobilized catalysts in photocatalytic reactors can simplify their operation and reduce their operational costs.

Several studies have compared the decomposition of substrates using suspended and immobilized catalysts (Li *et al*., 2010; Grieken *et al*., 2009; Scotti *et al*., 2009; Ochuma *et al*., 2007a; Cho *et al*., 2005; Ling *et al*., 2004; Mehrotra *et al*., 2005; Dijkstra *et al*., 2001). However, these studies reached different conclusions. Slurry systems were variously reported to be more efficient, less efficient, and as efficient as the immobilized systems.

To assist in the scaling-up of photocatalytic reactors, this study aims to establish the differences between the effects of suspended and immobilized catalysts on the decomposition of a substrate.

Preliminary experiments were carried out to confirm that the disappearance of phenol was only caused by photocatalytic degradation. To test this, phenol losses by evaporation, the time to reach the adsorption equilibrium, irradiation effects and photolysis rates were measured. The optimum catalyst loading conditions for the adopted configuration were then identified, and the reaction rate of the slurry batch reactor was determined. Measurements of the slurry catalyst were compared to those of the immobilized catalyst. Catalytic activity losses were also studied.

II. METHODS

All measurements presented in this work were repeated three times, and the averages of the observations are reported.

A. Materials and reactants

Experiments were carried out in a 1 L glass cylindrical reactor, which was jacketed, covered with aluminum foil and enclosed in a wooden box with a built-in fan.

Table 1: Literature values of phenol photocatalytic degradation using batch slurry reactors with TiO$_2$.

Author	UV Source	Reactor Volume	Initial Phenol Concentration	C_{cat}	k (min^{-1})	$\frac{k}{C_{cat}}$ ($\frac{L}{\min g_{cat}}$)
Chun *et al*., 2000	500 W	500 mL	100 mg L^{-1}	2.5 g L^{-1}	0.0448	0.01792
Peiró *et al*., 2001	125 W	100 mL	100 mg L^{-1}	1.5 g L^{-1}	0.099	0.066
Cesconetto, 2002	80 W	2 L	70 mg L^{-1}	1.0 g L^{-1}	0.282	0.282
Cesconetto, 2002	125 W	2 L	70 mg L^{-1}	1.0 g L^{-1}	0.016	0.016
Silva, 2007	125 W	1 L	50 mg L^{-1}	0.3 g L^{-1}	0.0013	0.00433
Chiou *et al*., 2008	400 W	0.8 L	48.9 mg L^{-1}	1.0 g L^{-1}	0.004	0.004
Azevedo *et al*., 2009	4 W	6 L	100 mg L^{-1}	2.3 g L^{-1}	0.0002	8.7 x 10^{-5}
Górska *et al*., 2009	1000 W	25 mL	19.7 mg L^{-1}	5 g L^{-1}	0.025	0.0005

The radiation source was a 125 W high-pressure mercury vapor lamp (Philips, 7.02 W m^{-2} at 365 nm) with a modified bulb that allowed pass-through of wavelengths greater than 350 nm. The lamp was positioned at a distance of 0.16 m above the liquid surface. TiO$_2$ (Degussa P-25, 80% anatase and 20% rutile, 50 m^2 g^{-1}) was used without prior treatment.

Phenol solutions (Vetec), NH$_4$OH (Synth), Na$_2$H PO$_4$.7H$_2$O/NaH$_2$PO$_4$.7H$_2$O (Synth), 4-aminoantipyrine (Sigma) and K$_3$[Fe(CN)$_6$] (Merck) were prepared with distilled and deionized water. All reactants were P.A. grade.

B. Phenol degradation in a slurry reactor
To achieve phenol adsorption equilibrium at the catalyst surface, the reactor was maintained without irradiation for 45 minutes after being loaded. Three milliliter samples were collected every 30 minutes with a syringe-catheter system. The samples were then centrifuged, diluted (1:10) and analyzed. The maximum reactor volume variation was 30 mL, which was considered negligible. The initial pHs of the solutions used in all experiments were measured to be 6.5.

To determine the time required to reach phenol adsorption equilibrium at the catalyst surface, experiments were carried out in the slurry reactor with bubbling air, 300 mg L^{-1} TiO$_2$ and 50 mg L^{-1} phenol and without irradiation.

To quantify the effects of evaporation, experiments were conducted in the absence of catalyst and radiation. Photolysis effects were evaluated by irradiating the reactor without the catalyst. Both experiments were conducted with bubbling air.

To determine the role of UV irradiation, a mercury lamp (Philips) and three black-light bulb lamps (Ecolume, Taschibra and Foxlux) were each used as radiation sources in the same apparatus. The peak emissions of these lamps were all measured at 365 nm with a Cole Parmer 9811-50 radiometer.

To determine the optimum catalyst loading parameters, experiments were conducted in the previously described experimental apparatus, using four different catalyst concentrations: 200, 300, 400 and 500 mg L^{-1}.

The initial concentration of phenol was 50 mg L^{-1} in all experiments.

C. Support preparation and catalyst immobilization
TiO$_2$ (P-25, Degussa) was immobilized onto glass plates (4.5 cm x 4.5 cm x 3 mm). The plates were blasted with glass particles to roughen their surfaces, and then treated with a 4 M NaOH solution for 24 hours. After rinsing with water, the plates were treated with a 2 M HCl solution for two hours, rinsed with distilled water and dried in an oven.

The suspension method was used to immobilize the catalyst onto the plate surface. A suspension of 2 g of TiO$_2$ in 100 mL of distilled and deionized water was prepared. This suspension was continuously agitated with a magnetic stirrer for 30 minutes to promote complete homogenization. The pretreated plates were placed into a container with a rough upper surface; then, the catalyst suspension was poured onto the plates, and the system was incubated for 30 minutes. The plates were removed from the suspension, dried at 100 °C for 20 minutes, and then, calcinated at 450°C for 30 minutes. The same methodology was repeated two additional times, yielding plates having three immobilized layers. Catalyst deposited onto the sides and bottom of the plate was removed, and the plates were weighed to determine the amount of TiO$_2$ deposited onto their surfaces.

The surface structure of the prepared catalyst film was examined using a scanning electron microscope (Jeol JSM 5800) operated at 10 kV and 50 μA. The plates' surface areas were evaluated by measuring the adsorption of methylene blue.

The stability of deposited film catalyst was evaluated by a 20h test, during which the plate with the immobilized catalyst was removed, dried in an oven and weighed every 2 hours. In this test the immobilized catalyst was placed at the reactor bottom in the horizontal position, and bubbling air was used for agitation. The plate was covered with 1 cm of pure water, and the plates were prepared with 0.10 ± 0.01g of catalyst.

D. Experiments using immobilized catalyst
The experiments were carried out like described in Part C, but using phenol solution instead of water, at an initial concentration of 50 mg L^{-1}. A 125 W mercury lamp (7.02 W m^{-2} at 365 nm) was used to irradiate the reactor. The reactor was placed into a wooden box cooled with a fan. For the deactivation studies, the samples were collected every 30 minutes over 3 hours, centrifuged and analyzed. The initial pH of the solutions used in all experiments was measured to be 6.5.

In all experiments presented in this work, the phenol concentration was measured using a colorimetric method based on the 4-aminoantipyrine reaction (APHA, 1998) that determines the total phenol content.

III. RESULTS AND DISCUSSIONS

A. Phenol degradation in a slurry reactor
i) Determination of evaporative losses
No significant phenol losses were observed in the 90-minute experiments, even in those with bubbled air flow. The results presented in Fig. 1 are the averages of three experiments (2.4% relative error). For comparison, a phenol degradation curve is also shown.

ii) Phenol adsorption at the catalyst surface
In order to exclude non-equilibrium effects from the photodecomposition rate measurements, the adsorption equilibration time was measured. The adsorption experiments showed a 5% variation in the phenol concentration (Fig. 1). Therefore, before all other experiments, the solution and catalyst were mixed without irradiation for 45 minutes to establish equilibrium. The equilibrium concentration was considered the initial concentration for the degradation reactions.

iii) The direct photolysis effect
Photocatalysis requires both irradiation and TiO$_2$. In the absence of the catalyst, there was no significant reduction in the phenol concentration after approximately 120

minutes of irradiation (Fig. 1). Phenol has two absorption peaks (210 and 270 nm), both in the UV-C spectrum and outside of the emission spectra of the lamps used eliminating the possibility of direct degradation (Philips, Technical Catalogue).

iv) Phenol photocatalytic degradation kinetics

In the present study, the model described by de Lasa *et al.* (2005) was adopted. This model is based on the Langmuir-Hinshelwood model, presented in Eq. 1, where r_{ph} is the rate of phenol disappearance in mg L^{-1} min^{-1}; $k_{ph-o-DHB}$, $k_{ph-p-DHB}$, $k_{ph-1,2,4-THB}$, $k_{ph-1,4-BQ}$, k_{ph-CO2} are the phenol specific reaction rates to ortho-dihydroxybenzene, para-dihydroxybenzene, 1,2,4 trihydroxybenzene, 1,4 benzoquinone and CO_2, respectively, in min^{-1}; C_{ph} is the phenol concentration in mg L^{-1}; K_j is the adsorption constant in L mg^{-1}; C_j is the concentration for each of the species present in the reaction in mg L^{-1}; and t is the time in minutes.

$$\frac{dC_{ph}}{dt} = r_{ph}$$
$$r_{ph} = \left[-(k_{ph \to o-DHB} + k_{ph \to p-DHB} + k_{ph \to 1,2,4-THB} + k_{ph \to 1,4-BQ} + k_{ph \to CO_2})C_{ph} \right] / (1 + \sum_{j=1}^{5} K_j C_j) \quad (1)$$

The colorimetric method was used to determine the total amounts of phenol and ortho- and meta-substituted phenols. The mechanism described by de Lasa *et al.* (2005) does not include formation of the meta-substituted compound. In this mechanism, formation of ortho-substituted compound is inhibited at pH 7 (similar to the pH used in the experiments described here). In the preliminary adsorption experiments in the present work (Fig. 1), phenol showed low adsorption to the catalyst surface. Because the phenol concentration is low, the $K_{ph}C_{ph}$ term in the denominator can be neglected, which reduces Eq. 1 to Eq. 2.

$$\frac{dC_{ph}}{dt} = -k_{exp} C_{ph} \quad (2)$$

Therefore, the experiments studying the phenol degradation were compared using k_{exp} as the response variable: k^s_{exp} for the slurry reactor and k^p_{exp} for the immobilized catalyst.
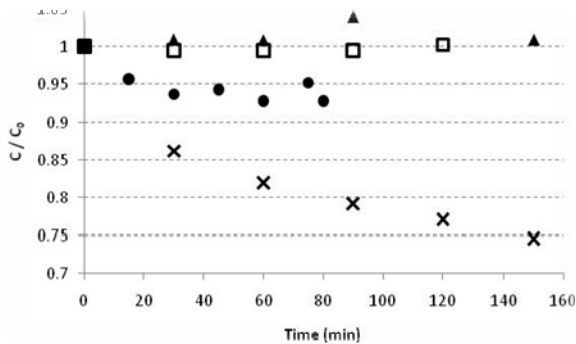
Figure 1: Preliminary experiments showing phenol losses through three pathways: (•) adsorption, (□) evaporation, (▲) photolysis and (x) phenol degradation (C_{ph} = 50 mg L^{-1}, V = 1 L, I_0 = 7.02 W m^{-2} and Q_{air}= 13 mL s^{-1}).
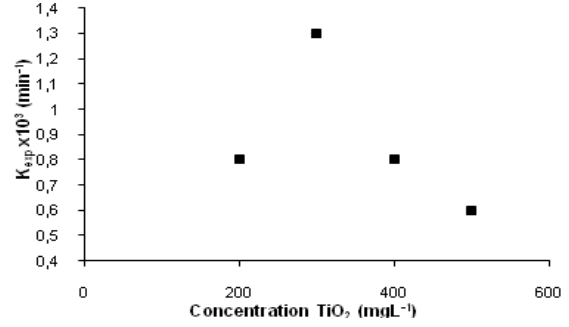
Figure 2: Effects of catalyst concentration (V = 1 L, C_0 = 50 mg L^{-1}, T = 30 °C, pH 6.5, Q_{air} = 13 mL s^{-1} and I_0 = 7.02 W m^{-2}).

v) The catalyst loading effect

A catalyst concentration of 300 mg L^{-1} was found to maximize the specific reaction rates (k^s_{exp}=0.0013 min^{-1}) (Fig. 2). Up to this maximum, higher catalyst concentrations increased the number of irradiated particles until all particles were illuminated. Higher catalyst concentrations increased the system's opacity and decreased the process efficiency (Gogate and Pandit, 2004).

vi) Irradiation effects.

To test the effects of irradiation, the incident radiation in the reactor was varied while all other conditions were held constant. The observed reaction rate had a nonlinear dependence on the irradiation (I) (Fig. 3). This behavior is similar that described in earlier reports (Herrmann, 2005; Ochuma *et al.*, 2007b); the relationship is linear for low incidence values, becomes proportional to $I^{0.5}$ as the irradiation increases and ultimately becomes constant with I. The subsequent phenol degradation experiments were performed with incident radiation of 0.7 mW cm^{-2}.

The experimental reaction rate constant k^s_{exp}, obtained using the optimum phenol degradation parameters (V = 1L, C_{ph} = 50 mg L^{-1}, T = 30 °C, C_{cat} = 300 mg L^{-1}, pH 6.5 and I = 7.02 W m^{-2}), was 0.0013 min^{-1} with an R^2 = 0.9922. This correlation indicates that the phenol photocatalytic degradation follows the expected pseudo-first order kinetics.

B. Phenol degradation using immobilized catalyst.

Figures 4a and 4b show the plate micrographs obtained by scanning electron microscopy. The surface was relatively uniform but contained cracks and pores ranging from approximately 0.2 to 0.7 μm in size. The immobilized catalyst surface area was determined to be 8.2 m^2 g^{-1} using methylene blue adsorption.

The stability of deposited film catalyst test showed that the catalyst mass loss after 20h was less than 1%, which enabling carried out long duration tests.

The suspended catalyst measurements were used in the immobilized catalyst experiments. It was assumed that phenol losses resulting from evaporation and photolysis could be ignored and that the dark time must be a minimum of 45 minutes. The catalyst was tested in the optimum conditions for the slurry reactor: pH 6.5 and I = 7.02 W m^{-2}. When the plate was used for the first time, the obtained k^p_{exp} was 0.0010 min^{-1}.
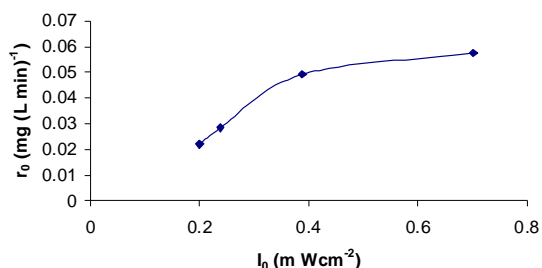
Figure 3: Phenol photocatalytic degradation rate dependence on incident irradiation.

Figure 4: Plates micrographs: (a) 40X and (b) 2000X.

C. Results comparison for the suspended and immobilized catalysts.

For batch reactors (de Lasa *et al*., 2005),

$$V \frac{dC_{ph}}{dt} = (r_{ph}^{''})A_{il} \; , \tag{3}$$

where C_{ph} is the phenol concentration (g cm^{-3}), V is the reactor volume (cm^3) occupied by phenol solution, $r_{ph}^{''}$ is the rate of phenol disappearance per illuminated area (g_{ph} min^{-1} cm^{-2}), A_{il} is the illuminated catalyst area (cm^2) and $(r_{ph}^{''}) = -k^{''}C_{ph}$, where $k^{''}$ is the specific reaction rate constant (cm min^{-1}). We can rewrite Eq. 3 as

$$\frac{dC_{ph}}{dt} = -\frac{k^{''}A_{il}}{V}C_{ph} = -k_{exp}C_{ph} \; , \tag{4}$$

giving

$$k^{''} = \frac{k_{exp}V}{A_{il}} \; . \tag{5}$$

Similarly, considering m_{cat} as the catalyst mass,

$$k^{'} = \frac{k_{exp}V}{m_{cat}} \; . \tag{6}$$

For both the immobilized and suspended catalysts, it is nearly impossible to determine the exact illuminated area or the corresponding illuminated mass. The aim of the present study is to achieve a practical relationship to assist in the scaling up of photocatalytic reactors. Therefore, the two approximations were used to calculate $k^{''}$ and $k^{'}$.

The incident radiation (W m^{-2}) on the catalyst was measured with a radiometer (positioned at the reactor center) and kept constant in all experiments. The constant $k^{''}$ was calculated using the illuminated area covered by the catalyst. This parameter corresponds to the area of the plate ($A_{il}^{p} = 20.25$ cm^2) when the catalyst is immobilized and, in the slurry reactor, to the area of the transverse section ($A_{il}^{s} = 78.5$ cm^2).

The constant $k^{'}$ was calculated using the total mass of the catalyst employed in the experiment and is a parameter that can be measured with precision. For both slurry and immobilized catalysts, the experiments were performed at optimum conditions. For slurry reactors, "optimum conditions" refer to the catalyst concentration, initial pH and irradiation levels chosen to give the maximum reaction rate ($C_{ph} = 50$ mg L^{-1}, T = 30°C, C_{cat} = 300 mg L^{-1}, pH= 6.5 and I = 7.02 W m^{-2}). For the immobilized system, "optimum conditions" refer to the immobilized catalyst mass (0.10 ± 0.01g) chosen to give maximum pollutant degradation.

The observed $k_{s}^{''}$ was 1.5 times greater than $k_{p}^{''}$, and the observed $k_{s}^{'}$ was two times larger than $k_{p}^{''}$.

Table 2 presents the calculated values of $k_{s}^{''}$, $k_{p}^{''}$, $k_{s}^{'}$ and $k_{p}^{'}$ for the photocatalytic degradation reactions of rhodamine B and tetracycline obtained in previous studies in this lab and those of phenol obtained in the current study. The ratio of $k_{s}^{'}$ to $k_{p}^{'}$ was between 2.1 and 5.3 for these pollutants.

Comparison of the results of this work to those found in the literature is not immediately straightforward. Working with DBU (1,8-diasabiciclo[5. 4. 0]undec-7-ene), Ochuma *et al.* (2007b) concluded that the immobilized catalyst was more efficient than the slurry system. However, their results were not obtained using the optimum conditions for each system, instead using identical catalyst mass concentrations. Ling *et al.* (2004), also working with identical catalyst mass concentrations, concluded that the two systems gave the same performance in phenol degradation. The Dijkstra *et al.* (2001) experiments for formic acid showed that the slurry system was four times more efficient than the immobilized one.

D. Deactivation of the immobilized catalyst

Significant catalyst deactivation was observed in the immobilized-catalyst systems. Phenol degradation generated a product that was deposited onto the immobilized catalyst surface, giving it a brown color. This deposit was not observed in the slurry reactor due to agitation. Similarly, other authors (Grzechulska and Morawski *et al*., 2003; Inazaki and Bidoia, 2004) found a dark deposit on the catalyst surface during phenol photocatalytic degradation.

The mechanism of this catalyst deactivation was investigated. TiO$_2$ was immobilized onto glass plates and exposed to parallel liquid flow across the plate surface. The results are shown in Table 3. Catalyst activity decreased during irradiation, and a change in the catalyst surface color was visible after a short period.

Table 3 shows the value k_{exp}^{p} and $k_{p}^{'}$ obtained when the standard phenol photocatalytic degradation reaction was performed several times with the same plate. After

24 hours of reaction, k_{exp}^p and $k_p^{'}$ were 60% its initial values.

IV. CONCLUSIONS

In this work, the TiO_2-catalyzed photocatalytic degradation of phenol in a slurry reactor was studied. Phenol degradation followed pseudo-first order kinetics with a specific reaction rate of 0.0013 min^{-1} under conditions of 30°C, initial phenol concentration of 50 mg L^{-1}, 300 mg L^{-1} of catalyst, irradiation of 7.02 W m^{-2} and 1 L reactor volume. The preliminary experiments showed that evaporation and photolysis were negligible as sources of phenol degradation. It was found that phenol has low adsorption onto the catalyst surface, and a dark time of 45 minutes should precede degradation experiments.

Defining $k_s^{'} = k_{exp}^s / C_{cat}$ and $k_p^{'} = (k_{exp}^p / m_{cat})V$, the ratio $k_s^{'} / k_p^{'}$ was between 2.1 and 5.3 for rhodamine B, tetracycline and phenol.

Significant deactivation was observed with the immobilized catalyst. After 24 hours of reaction, kinetics constants were 60% its original values.

NOMENCLATURE

A_{il} illuminated area (cm^2)
C   concentration (g mL^{-1})
$k_{ph-o-DHB}$ phenol specific reaction rates to ortho-dihydroxybenzene (min^{-1})

$k_{ph-p-DHB}$ phenol specific reaction rates to para-dihydroxybenzene (min^{-1})
$k_{ph-1,2,4-HB}$ phenol specific reaction rates to 1,2,4 trihydroxybenzene (min^{-1})
$k_{ph-1,4-BQ}$ phenol specific reaction rates to benzoquinone (min^{-1})
k_{ph-CO2} phenol specific reaction rates to CO_2 (min^{-1})
k_{exp} experimental specific reaction rate (min^{-1}).
k"   specific reaction rate based on the illuminated area $(k^{"} = k_{exp}V/A_{il})$ (cm min^{-1})
k'   specific reaction rate based on the catalyst mass $(k^{'} = k_{exp}V/w)$ (cm^3 min^{-1} g^{-1})
K_j adsorption constant (L mg^{-1})
m   mass (g)
r_{ph} rate of phenol disappearance (g L^{-1} min^{-1})
$r_{ph}^{"}$ rate of phenol disappearance based on the illuminated area (g$_{ph}$ min^{-1} cm^{-2})
$r_{ph}^{'}$ rate of phenol disappearance based on the catalyst mass (g$_{ph}$ min^{-1} g^{-1})
t   time (min)
V   reactor volume occupied for phenol (cm^3)
SUBSCRIPTS
P   indicates immobilized catalyst
Ph   indicates phenol
S   indicates slurry reactor
Cat   indicates catalyst

Table 2: The calculations used for the comparison between the batch reactors with the immobilized and suspended catalysts.

		Rhodamine B	Tetracycline	Phenol
Slurry	Occupied reactor volume, V (cm^3)	900	900	900
	Catalyst concentration, C_{cat} (g cm^{-3})	0.3×10^{-3}	0.6×10^{-3}	0.3×10^{-3}
	Illuminated area, A_{il}^s (cm^2)	78.50	78.50	78.50
	365 nm irradiation (mW cm^{-2})	3.8	3.3	0.7
	Initial concentration (g cm^{-3})	50×10^{-6}	50×10^{-6}	50×10^{-6}
	pH	8.0	4.0	6.5
	k_{exp}^s (min^{-1})	0.0097	0.0170	0.0013
	$k_S^{"} = k_{exp}^s V / A_{il}^s$ (cm min^{-1})	0.1112	0.1949	0.0149
	$k_s^{'} = k_{exp}^s / C_{cat}$ (cm^3 / min g$_{cat}$)	32.33	28.33	4.33
Immobilized	Occupied reactor volume V (cm^3)	100	100	200
	Mass of immobilized catalyst, m_{cat} (g)	0.059	0.0540	0.0960
	365nm irradiation (mW cm^{-2})	0.7	4.5	0.7
	Illuminated area A_{il}^P (cm^2)	20.25	20.25	20.25
	Initial concentration (g cm^{-3})	20×10^{-6}	30×10^{-6}	50×10^{-6}
	pH	8.0	4.0	6.5
	k_{exp}^p (min^{-1})	0.0036	0.00425	0.0010
	$k_P^{"} = k_{exp}^p V / A_{il}^P$ (cm min^{-1})	0.0178	0.0210	0.0099
	$k_p^{'} = (k_{exp}^p / m_{cat})V$ (cm^3 / min gTiO$_2$)	6.10	7.87	2.08
Relationship	$k_s^{"} / k_p^{"}$	6.25	9.28	1.50
	$k_s^{'} / k_p^{'}$	5.30	3.60	2.08
References		-	Soares *et al.*, 2007	Buth, 2009	Silva, 2007

Table 3: The specific rate constants obtained when the immobilized catalyst was used repeatedly in phenol degradation.

t (h)	0 - 3	3 - 6	6 - 9	9 - 15	15 - 18	18 - 24
$k_{exp}^p \times 10^3$ (min^{-1})	1.0	0.9	0.9	0.7	0.6	0.6
$k_p^{'}$ (cm^3 / min gTiO$_2$)	2.08	1.87	1.87	1.46	1.25	1.25

REFERENCES
APHA, *Standard Methods for the examination of water and wastewater*, American Water Works Association, Washington (1998).

Azevedo, E.B., A.R. Torres, F.R.A. Neto and M. Dezotti, "TiO$_2$-photocatalyzed degradation of phenol in saline media in an annular reactor: hydrodynam-ics, lumped kinetics, intermediates, and acute toxicity," *Brazilian Journal of Chemical Engineering*, **26**, 75-87 (2009).Buth. D.F., *Degradação fotocatalítica da tetraciclina em solução aquosa empregando TiO$_2$ suportado,* M. Sc. Thesis, Universidade Federal do Rio Grande do Sul, Brazil, Available in http://hdl. handle.net/10183/18992 (2009).

Cesconetto, G.N., *Decomposição de fenol em efluente da indústria de papel e celulose por fotocatálise heterogênea*, M. Sc. Thesis, Universidade Federal de Santa Catarina (2002).

Chiou, C.H., C.Y. Wu and R.S. Juang, "Photocatalytic degradation of phenol and m-nitrophenol using ir-radiated TiO$_2$ in aqueous solutions," *Separation and Purification Technology*, **62**, 559-564 (2008).

Chun, H., W. Yizhong, and T. Hongxiao, "Destruction of phenol aqueous solution by photocatalysis or direct photolysis," *Chemosphere*, **41**, 1205-1211 (2000).

Cho, I.H., J.H. Park and Y.G. Kim, "Oxidative degradation and toxicity reduction of trichloroethylene (TCE) in water using TiO$_2$/solar light: Comparative study of TiO$_2$ slurry and immobilized systems". *Journal of Environmental Science And Health Part A-Toxic/Hazardous Substances & Environmental Engineering,* **40,** 1033-1044 (2005).

de Lasa, H., B. Serrano and M. Salaices, *Photocatalytic Reaction Engineering*. Springer Science + Business (2005).

Dijkstra, M.F.J., A. Michorius, H. Buwalda and H.J. Panneman, "Comparison of the efficiency of immobilized and suspended systems in photocatalytic degradation," *Catalysis Today*, **66**, 487–494 (2001).

Gogate, P.R. and A.B. Pandit, "A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions," *Advances in Environmental Research,* **8**, 501-551 (2004).

Gorska, P., A. Zaleska and J. Hupka, "Photodegradation of phenol by UV/TiO$_2$ and Vis/N,C-TiO$_2$ processes: Comparative mechanistic and kinetic studies," *Separation and Purification Technology*, **68**, 90-96 (2009).

Grieken R.V., J. Marugán, C. Sordo and C. Pablos, "Comparison of the photocatalytic disinfection of E. coli suspensions in slurry, wall and fixed-bed reactors," *Catalysis Today*, **144**, 48–54 (2009).

Grzechulska, J. and A.W. Morawski, "Photocatalytic labyrinth flow reactor with immobilized P25 TiO$_2$ bed for removal of phenol from water," *Applied Catalysis B-Environmental*, **46**, 415-419 (2003).

Herrmann, J.M., "Heterogeneous photocatalysis: State of the art and present applications," *Topics in Catalysis*, **34**, 49-65 (2005).

Inazaki, T.H. and E.D. Bidoia, "Tratamento fotocatalítico de efluente simulado contendo fenol utilizando TiO$_2$ Degussa," *17° Reunião Anual do Instituto Biológico de São Paulo* (2004).

Li, D., K. Xiong, W. Li and Z.H. Yang, "Comparative Study in liquid-fase heterogeneous photocatalysis: model for photoreactor scale-up," *Industrial and Engineering Chemistry Researsh*, **49**, 8397-8405 (2010).

Ling, C.M., A.R. Mohamed and S. Bhatia, "Performance of photocatalytic reactors using immobilized TiO$_2$ film for the degradation of phenol and methylene blue dye present in water stream," *Chemosphere*, **57**, 547–554 (2004).

Mehrotra, K., G.S. Yablonsky and A.K. Ray, "Macro kinetic studies for photocatalytic degradation of benzoic acid in immobilized systems," *Chemosphere,* **60,** 1427–1436 (2005).

Ochuma, I.J., R.P. Fishwick, J. Wood and J.M. Winterbottom, "Photocatalytic oxidation of 2,4,6-trichlorophenol in water using a cocurrent downflow contactor reactor (CDCR)," *Journal of Hazardous Materials*, **144**, 627-633 (2007a).

Ochuma I.J., O.O. Oluwapomile, R.P. Fishwick and S. Pollington, "Three-phase photocatalysis using suspended titania and titania supported on a reticulated foam monolith for water purification," *Catalysis Today,* **128**, 100–107 (2007).

Peiro, A.M., J.A. Ayllon, J. Peral and X. Domenech, "TiO$_2$-photocatalyzed degradation of phenol and ortho-substituted phenolic compounds," *Applied Catalysis B-Environmental*, **30**, 359-373 (2001).

Philips, *Technical Catalogue HPLN Lamps – Mercury*. Available at: http://www.luz.philips.com/archives /pt_lamps_hid_hpln.pdf.

Scotti, R., M. D'Arienzo, F. Morazzoni and I.R. Bellobono, "Immobilization of hydrothermally produced TiO$_2$ with different phase composition for photocatalytic degradation of phenol," *Applied Catalysis B: Environmental*, **88**, 323–330 (2009).

Silva, F.V., *Aplicação da fotocatálise heterogênea para degradação de benzeno e fenol em um reator contínuo do tipo labirinto*, M. Sc. Thesis, Universidade Federal do Rio Grande do Sul, Brazil, Available in http://hdl.handle.net/ 10183/10356 (2007).

Soares, E.T., M.A. Lansarin and C.C. Moro, "A study of process variables for the photocatalytic degradation of rhodamine B," *Brazilian Journal of Chemical Engineering*, **24**, 29-36 (2007).