PHOTOCATALYSIS AS A TERTIARY TREATMENT FOR PETROLEUM REFINERY WASTEWATERS

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Abstract - Photocatalysis has been used as tertiary treatment for petroleum refinery wastewaters to comply with the regulatory discharge limits and to oxidize persistent compounds that had not been oxidized in the biological treatment. The wastewater is generated by the refinery and directly discharged into the Guanabara Bay (Rio de Janeiro). Although BOD removal is high, a residual and persistent COD, besides a somewhat high phenol content remains. Three photocatalysts were tested — TiO_2 (Aldrich), ZnO (Aldrich), and TiO_2 (P25, Degussa) — the third being the most active. The optimized conditions obtained with an experimental design were 3.0 g L^{-1} TiO_2 and pH 6.3. The use of hydrogen peroxide (H_2O_2) showed no beneficial effect. Removal of 93% of phenols, 63% of dissolved organic carbon (DOC), and more than 50% of oil and grease (OG) were achieved in the photocatalytic process, improving the quality of the treated wastewater.
Keywords: Photocatalysis; TiO_2; Hydrogen peroxide; Petroleum; Refinery; Wastewater.

INTRODUCTION

A stricter control through environmental regulations and legislation has driven the great effort to seek alternative technologies, which have the following important features: enhanced efficiency, self-sustainability, and absence of hazardous wastes. In this scenario, photocatalysis, an oxidative process, has been emphasized, which in many cases, has resulted in the total mineralization of persistent organic compounds.

Photocatalysis is being applied to the elimination of several pollutants (e.g., alkanes, alkenes, phenols, aromatics, pesticides) with great success. In many cases, total mineralization of the organic compounds has been observed (Linsebigler et al., 1995,

Hoffmann et al., 1995, Bekbolet and Balcioglu, 1996, Shiavello, 1993).

Several photocatalysts, such as CdS, Fe_2O_3, ZnO, WO_3, and ZnS, have been studied, but the best results have been achieved with TiO_2 P25 supplied by Degussa (Legrini et al., 1993).

The addition of small concentrations of hydrogen peroxide (H_2O_2), to photocatalytic systems may enhance the process efficiency. At higher concentrations, hydrogen peroxide was found to have an inhibiting effect on photocatalytic reactions (Dionysiou et al., 2004). Hydrogen peroxide can accelerate the reaction rate by capturing electrons, reacting with excess oxygen, or absorbing light with wavelengths shorter than 310 nm. In all situations described, •OH radicals, which are critical for the

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process due to their high reactivity, are generated (Rajeshwar, 1995, Herrmann et al., 1993).

The wastewaters of an oil refinery are the waters resulting from washing the equipment used in the process, undesirable wastes, and sanitary sewage (Stepnowski, 2002). These effluents have high oil and grease contents, besides other organic compounds in solution. These pollutants form a residual COD that may pose serious toxic hazards to the environment. The effluents are quite variable, depending on the type of oil being processed, process configuration, and plant operation procedures. Therefore, defining the typical composition for these effluents is troublesome.

In the present work, photocatalysis has been used as tertiary treatment for petroleum refinery wastewaters in order to reduce the amount of pollutants to the level of the regulatory discharge limits and to oxidize persistent compounds that had not been oxidized in the biological treatment. The treatment sequence used by the refinery

(REDUC/PETROBRAS, a Brazilian oil refinery) is oil/water separation followed by a biological treatment. Although the process efficiency in terms of BOD removal is high, a residual and persistent COD, besides somewhat high phenol content, remains. The refining capacity of the refinery is 41,000 m^3/day, generating 1,100 m^3/h of wastewater, which are discharged directly into the Guanabara Bay (Rio de Janeiro).

MATERIALS AND METHODS

Wastewater

The wastewater was collected at the exit pipe of a series of aerated lagoons and stored at 4ºC with a pH < 2. A characterization of the wastewater, along with the pollutant limits imposed by the Rio de Janeiro Environmental Agency (FEEMA), is presented in Table 1.

**Table 1: Wastewater characterization and limits imposed by
the Rio de Janeiro Environmental Agency (FEEMA).**

Parameter	Average Concentration of Wastewater (mg L^{-1})	Maximum Allowed Concentration (mg L^{-1})
pH	6.7*	5 - 9*
COD (filtered)	200	250
DOC	20	-
Oil and Grease	23	20
Ammonia	70	5
Total Phenols	3.7	0.2

* dimensionless

Reagents

All chemicals used were at least reagent grade and were used as received. Three different photocatalysts were tested: from Aldrich, ZnO and TiO$_2$ (BET surface areas of 1.7 and 8.3 $m^2 g^{-1}$); from Degussa, TiO$_2$ P25 (30 nm particle size and 50 ± 15 $m^2 g^{-1}$ BET surface area). Solutions were prepared with distilled water.

Photocatalytic Experiments

The first set of experiments was carried out in an open 250 mL reactor containing 60 mL of wastewater. In the second set of experiments, a Pyrex® annular reactor containing 550 mL of wastewater was used (De Paoli and Rodrigues,

1978), as shown in Figure 1. The reaction mixtures inside the reactors were maintained in suspension by magnetic stirring. In all experiments, air was continuously bubbled through the suspensions. A 250 W Phillips HPL–N medium pressure mercury vapor lamp (with its outer bulb removed) was used as the UV-light source (radiant flux of 108 J·m^{-2}·s^{-1} at $\lambda > 254$ nm). In the first set of experiments, the lamp was positioned above the surface of the liquid at a fixed height (12 cm). In the second one, the lamp was inserted into the well, as depicted in Figure 1. All experiments were performed at 25 ± 1°C. The catalyst concentration ranged from 0.5 to 5.5 g L^{-1} and the initial pH from 3.5 to 9. In order to remove photocatalyst particles before analyses, samples were filtered through 0.45 μm pore size cellulose acetate filters.
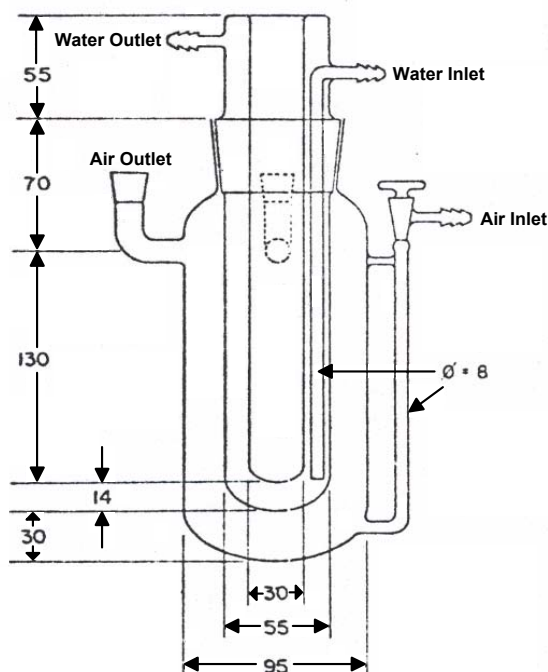
Figure 1: Pyrex® annular reactor. Dimensions in mm.

Experimental Design

An experimental design, $OA_{36}(3^3)$, with ten repetitions of the central point, has been made to study the effect of the addition of hydrogen peroxide (Box, 1954). The variables and their respective levels (–1, 0, and +1) were pH (1.5, 6.3, and 11.0), photocatalyst (TiO$_2$ P25 Degussa) concentration (0.5, 3.0, and 5.5 g L^{-1}), and hydrogen peroxide concentration (5, 30, and 55 mmol L^{-1}). The irradiation time was always 60 minutes. A quadratic model without second-order interactions was fit to the experimental data.

Analyses

The UV spectra of the samples were obtained by scanning (400 through 189 nm) them in a Varian Carry 1E UV-Visible spectrophotometer (Bessa et al., 1999, 2001). The integrated areas under the scanning spectra were then calculated. Those areas represent semi-quantitatively the concentration of organic compounds having conjugated double and/or triple bondings (which includes all aromatic compounds). Chemical oxygen demand (COD) was measured according to the closed reflux method (APHA, 1992a) and dissolved organic carbon (DOC) was measured in a Dhormann® DC–190 TOC

analyzer. Degradation of the phenols was followed by determination of the concentration of unreacted phenol by a colorimetric method (APHA, 1992b) on a HACH DR/2000 visible spectrophotometer. The ammonia content was determined by a colorimetric method (Merck Spectroquant®14752). The oil and grease was determined according to the Soxhlet extraction method (APHA, 1992c).

RESULTS AND DISCUSSION

Screening Experiments

Initially, a series of screening experiments was performed in order to determine the best initial pH and photocatalyst concentration. Three different solids were tested — ZnO and TiO$_2$ (both supplied by Aldrich) and TiO$_2$ P25 from Degussa. Table 2 summarizes the best results achieved for each solid in terms of total phenol degradation, as this parameter showed the greatest departure from the limit imposed by the environmental agency. Control experiments in the dark showed no significant changes in the wastewater.

It can be seen that the TiO$_2$ supplied by Aldrich is less active than the other two. This fact had already been reported elsewhere (Bessa et al., 1999, 2001).

ZnO was twice as active, but its major drawback is that severe losses of solid to the solution (solubilization) were observed during the experiments. Undoubtedly, the TiO_2 P25 was the most active photocatalyst (approximately 5 and 2.5 times more active than the TiO_2 and ZnO supplied by Aldrich, respectively). Moreover, it offers two other advantages: less photocatalyst can be used (3 g L^{-1} compared to 5 g L^{-1}) and the pH is already near the effluent discharged, requiring no adjustment of pH. The fact that the best pH was at the zero charge point (pH_{zcp}), where the TiO_2 surface is neutral

(Kormann et al., 1991), is probably related to the non polar nature of the majority of the organic pollutants (alkanes) in the wastewater (Tanaka and Saha, 1994, Watts et al., 1994), although the concentration of alkanes was not measured.

Another quite interesting finding is depicted in Figure 2. Regardless of the initial pH, the final effluent tends to neutrality, which is extremely desirable due to the discharge limits. The reason for this behavior is not clear, as pH tends to decrease during oxidation reactions due the formation of acids

Table 2: Best results achieved (in terms of photocatalyst concentration and initial pH) for total phenol degradation for a 60 min irradiation time.

Photocatalyst	Supplier	$C_{Photocatalyst}$ (g L^{-1})	pH	Total Phenol Residual (%)	Degradation Enhancement*
TiO_2	Aldrich	5.0	5.5	35.2	1
ZnO	Aldrich	5.0	3.5	16.7	2
TiO_2 P25	Degussa	3.0	6.3	6.98	5

*The parameter *Degradation Enhancement* is compared to the efficiency obtained using the TiO_2 supplied by Aldrich as the photocatalyst.
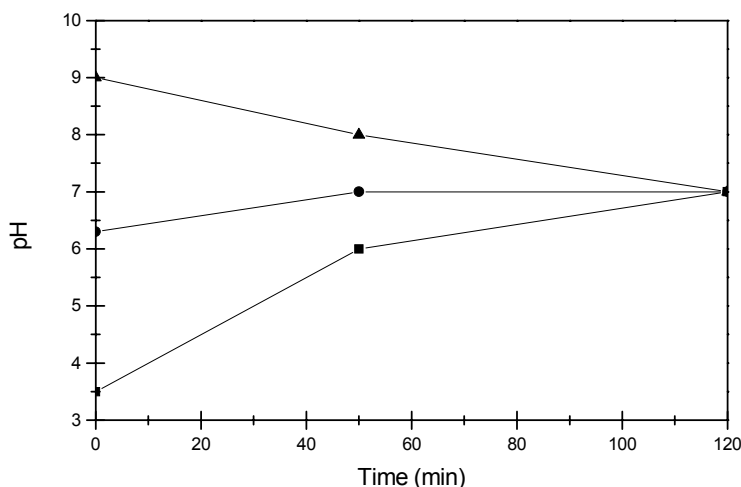

Figure 2: Evolution of pH during photocatalysis (TiO_2 P25 at 3.0 g L^{-1}) at different initial pHs (▲ 9.0, ● 6.3, and ■ 3.5).

Experimental Design

From the ten repetitions of the central point, the overall experimental errors (experiments + analyses) for the UV area and phenol content were estimated at approximately 0.8 and 0.23 mg L^{-1}, respectively. Those errors were quite a bit smaller than the values measured.

The response surfaces obtained are shown in

Figure 3. It can be seen that the highest degradations were achieved with the lower hydrogen peroxide concentration (5 mmol L^{-1}), which is in good agreement with the literature (Dionysiou et al., 2004, Schiavello, 1993). Nevertheless, the enhancement of degradation obtained by the use of hydrogen peroxide was negligible. The degradations at the response surface minima are summarized in Table 3.
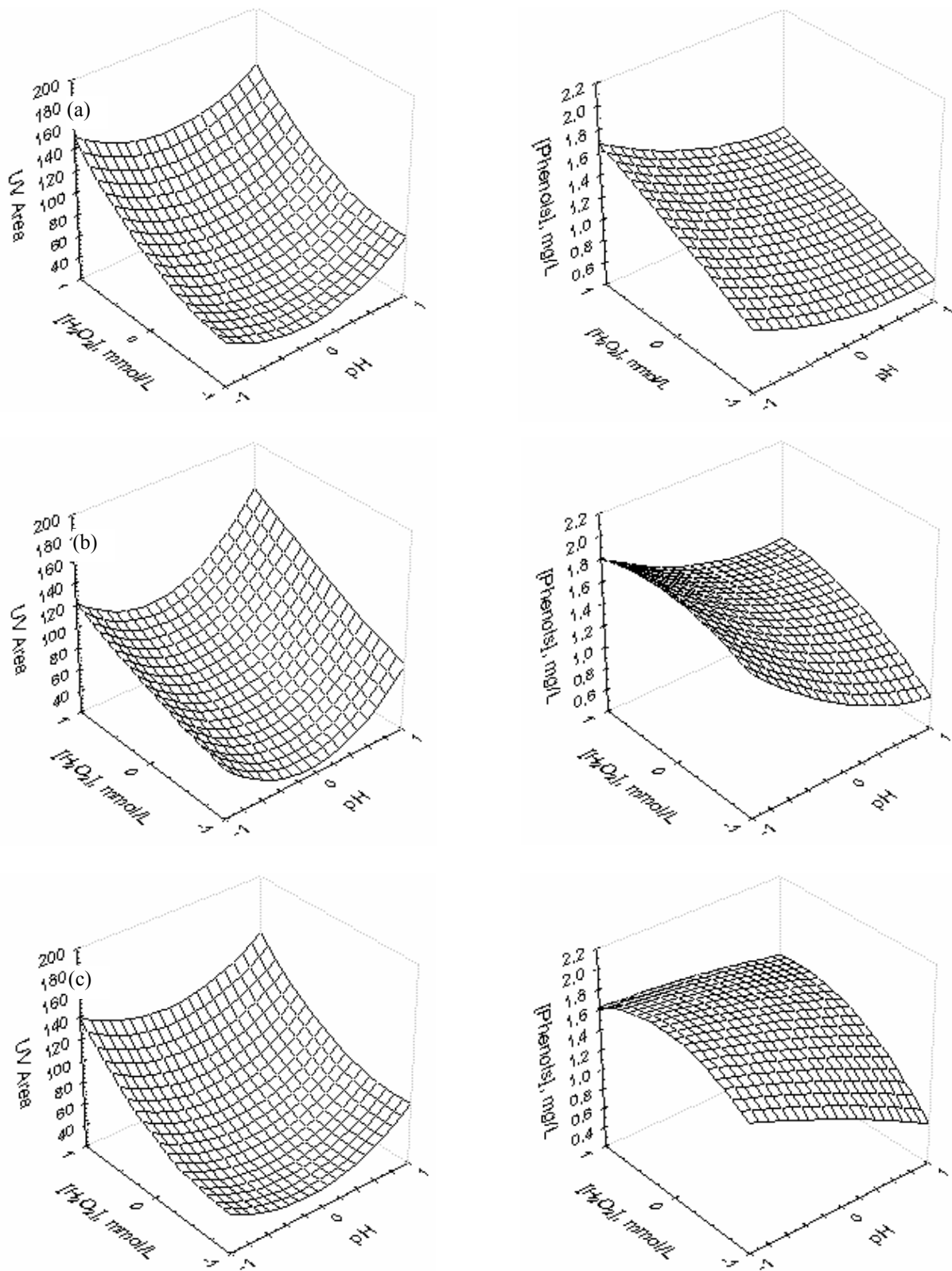
Figure 3: Response surfaces for UV area and phenol concentration. TiO$_2$ (P25 Degussa) concentration: (a) 0.5 g L^{-1}, (b) 3.0 g L^{-1}, and (c) 5.5 g L^{-1}.

Table 3: Degradation (%) at the response surface minima.

TiO$_2$*, g L^{-1}	Degradation (%)	
	UV Area	Phenols, mg L^{-1}
0.5	73	83
3.0	79	81
5.5	71	83

* P25 Degussa.

Regarding the UV area, it can be seen that the use of 3.0 g L^{-1} of TiO$_2$ resulted in a somewhat better degradation and that a pH close to 7 was the best one.

Regarding phenol content, the TiO$_2$ concentration did not significantly affect the degradation process. On the other hand, the use of a basic medium provided the best results.

Therefore, the following experiments were performed using 3.0 g L^{-1} of TiO$_2$ and pH 6.3. Although this is not the best pH for phenol removal, it was estimated that degradation would decrease by only 10% with the neutral pH. It is noteworthy that the best experimental conditions obtained by the experimental design confirmed the ones found during the screening experiments.

Experiments Under the Optimized Conditions

As can be seen in Table 1, the COD/DOC ratio was approximately 10. In fact, this wastewater has a high content of sulfide, polisulfide, sulfonate, and chloride ions, ammonia, etc. Those species are readily oxidized in the COD test. Therefore, the DOC parameter was chosen in order to observe degradation of the organic matter.

The results obtained for phenol degradation and degradation of organic matter are shown in Figure 4.

This wastewater showed insignificant changes when irradiated with UV light (photolysis).

The use of TiO$_2$/UV (photocatalysis) resulted in a significant increase in phenol removal (93%, one hour). The DOC curve did not show the previous behavior. In fact, 56% of the DOC was removed in the first hour. This is probably due to the fact that photocatalysis is a much more oxidative process than H$_2$O$_2$/UV, so the reactions that take place are much faster.

Moreover, the increase in degradation obtained by the use of H$_2$O$_2$ coupled with photocatalysis was marginal. Therefore, its use is not recommended for this kind of wastewater, as no significant enhancement of removal is obtained for photocatalysis and costs are increased.

Another important finding is that there is no need to treat the wastewater for a period of time longer than one hour, as the results achieved change little after this time.
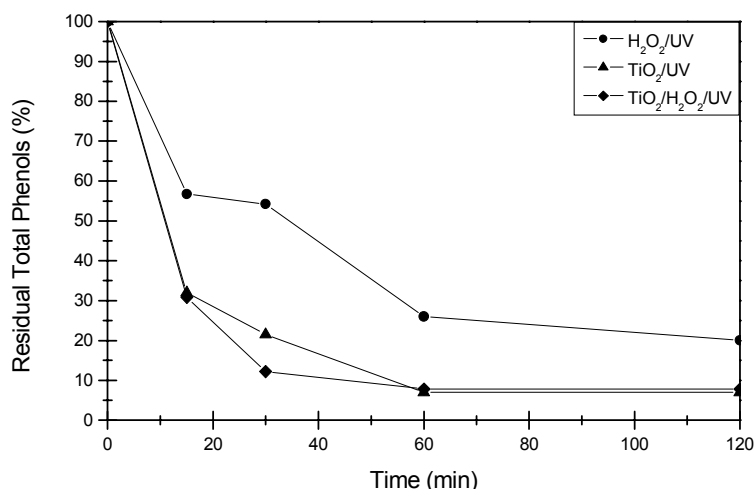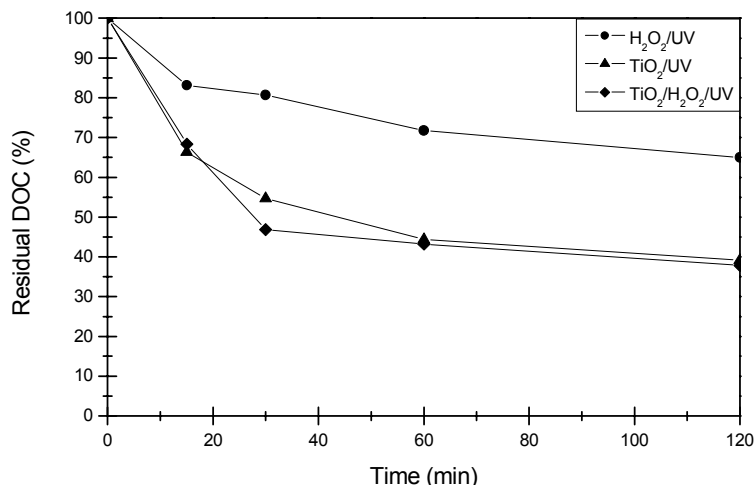
Figure 4: Results for different oxidation processes under the optimized conditions.

## Experiments With the Pyrex® Annular Reactor

This set of experiments was intended to assess the performance of photocatalysis, using only the near-UV and visible wavelengths of the lamp, which is compatible with solar applications. As the shape changed, three different concentrations of photocatalyst were tested (0.5, 3.0, and 5.5 g L^{-1}). As can be seen in Figure 5, the amount of TiO_2 had no significant effect on the process.

When the two sets of experiments are compared, it can observed that performance of the Pyrex® annular reactor is better than that of the open one, as depicted in Figure 6. The removal of phenols was quite the same, but the DOC removal obtained was 63%. This is probably due to a better use of the photons (as the lamp is inside the reactor) and a larger fraction of photocatalyst being illuminated. Therefore, it seems that the use of helio-photocatalysis with this wastewater would be feasible.

Final Wastewater Characterization

After photocatalytical treatment of the wastewater in the Pyrex® annular reactor, under the optimized conditions, its general quality was significantly improved. The results are summarized in Table 4. It is noteworthy that phenol and oil and grease contents, which had been above the legislated limits, were reduced to discharge levels. Also, more than half of the DOC was removed from the wastewater. Finally, an insignificant amount of ammonia was removed (not more than 10%).
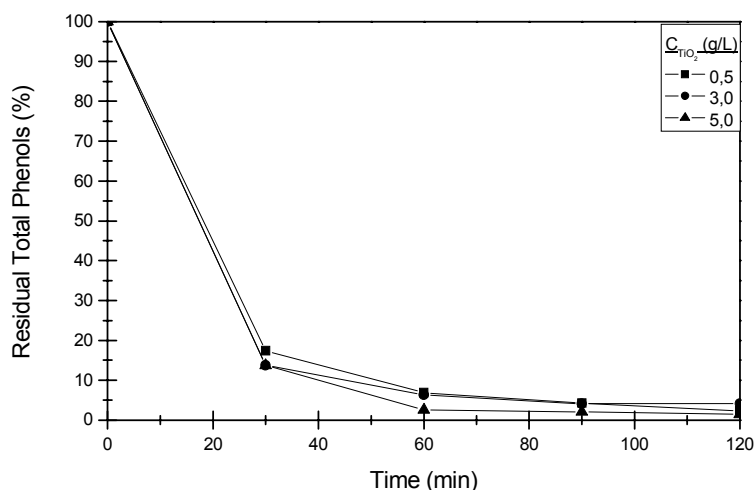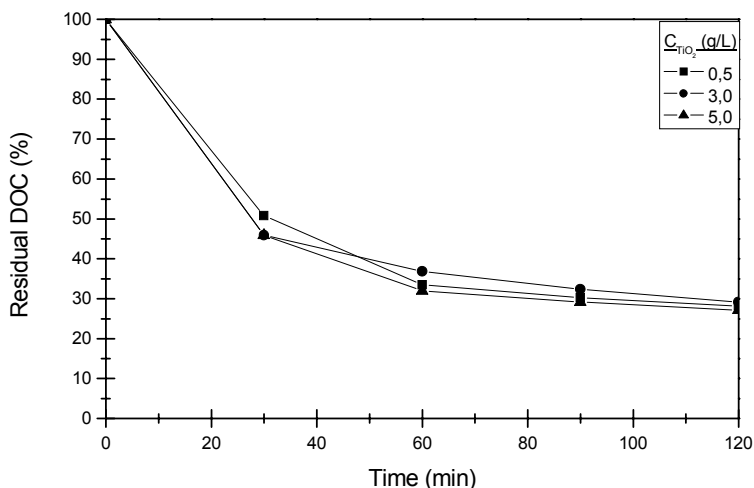
Figure 5: Pyrex® reactor: the effect of TiO_2 concentration on the degradation process.
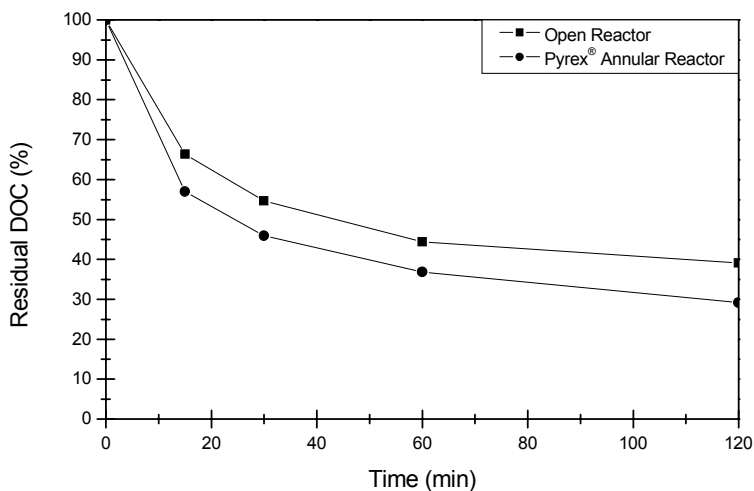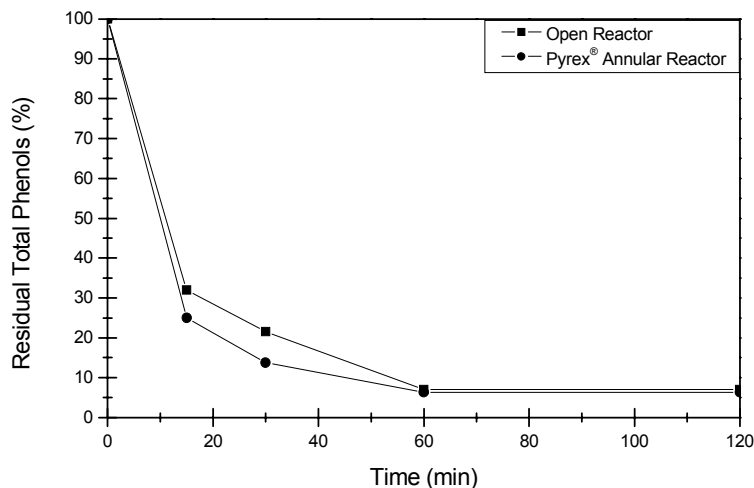

Figure 6: Comparison between the performances of the reactors.

Table 4: Wastewater characterization after the photocatalytic treatment under optimal conditions.

Parameter	Before Photocatalysis	After Photocatalysis
pH	6.7	7
DOC*	20	7
Oil and Grease*	23	< 10
Ammonia*	70	63
Total Phenols*	3.7	0.2

* In mg L^{-1}.

CONCLUSIONS

The order of photocatalytic activity for the three solids tested was TiO_2 (Aldrich) < ZnO (Aldrich) < TiO_2 (P25, Degussa). Severe losses to the solution were observed with the use of ZnO.

The use of hydrogen peroxide to enhance the oxidative process was beneficial for photolysis but had no significant effect for photocatalysis.

The optimized pH (6.3) is quite interesting for process operation, since it is very close to the final pH required for effluent discharge.

High rates of removal were achieved for phenols, oil and grease, and dissolved organic carbon. Therefore, photocatalysis (TiO_2/UV) can be applied successfully to petroleum refinery wastewaters, attaining the quality standards required for final disposal.

ACKNOWLEDGMENTS

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