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THE EFFECT OF METAL OXIDES ON THE REFINERY EFFLUENT TREATMENT

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ABSTRACT

Metal Oxides (Titania TiO_2, and Calamine (ZNO)) have been used as tertiary treatment for Refinery Effluent treatment and wastewaters to comply with the regulatory discharge limits and to oxidize persistent compounds that had not been oxidized in the biological treatment. The wastewater was provided by the Bandar Abbas Refinery. Although BOD removal is high in this plant, a residual and persistent COD (Chemical Oxygen Demand), besides a somewhat high phenol content remains. Three catalysts were tested TiO2 (Aldrich), ZnO (Aldrich), and TiO_2 (P25, Degussa) by the UV radiation, the third being the most active. The optimized conditions obtained with an experimental design were 3.0 (g/L) TiO_2 and pH=6.3. The use of hydrogen peroxide (H_2O_2) showed no beneficial effect. Removal of 93% of phenols, 56% of dissolved organic carbon (DOC), and more than 50% of oil and grease (OG) were achieved in the catalytic process with UV radiation, improving the quality of the treated wastewater.

Key words: Titania, Calamine; Hidrogen peroxide; Refinery; Effluent treatment; Wastewater

INTRODUCTION

Enhanced efficiency, self-sustainability, and absence of hazardous wastes and stricter control through environmental regulations and legislation have driven the great effort to seek alternative technologies. Photocatalysis, an oxidative process, has been emphasized, which in many cases, has resulted in the total mineralization of persistent organic compounds (Legrini *et al*., 1993; Herrmann *et al*., 1993).

Photocatalysis is being applied for the elimination of several pollutants (e.g., alkenes, alkenes, phenols, aromatics, pesticides) with great success. In many cases, total mineralization of the organic compounds has been observed (Linsebigler *et al*.,1995; Bekbolet *et al*.,1996; Schiavello, 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. 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 (Rajeshwar, 1995)

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 process due to their high reactivity, are generated .

The wastewaters of an oil refinery are the waters resulting from washing the equipments used in

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the process, undesirable wastes, and sanitary sewage (Stepnowski *et al*., 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. 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 (Salahi *et al*., 2010). The treatment sequence used by the refinery (B.Rifinery IRAN) is oil/water separation followed by a biological treatment.(Sarrafzadeh *et al*., 2010). 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 51,000 m^3/day, generating 2100 m^3/h of wastewater, which are discharged directly into the Persian Gulf.

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. The wastewater characterization, along with the pollutant limits imposed by the Iran Department of Environment (DOE), are presented in Table 1.

Table1: Wastewater characterization and limits imposed by DOE

Parameters	Average Concentration of wastewater(mg/L)	Concentration (mg/L)
pH	6.7	6
COD(filtrated)	250	200
DOC	28	-
Oil and grease	27	15
Ammonia	26	5
Phenol	3.7	0.2

Reagents

All chemicals used were at least reagent grade and were used as received. Three different photo catalysts were tested: from Aldrich, ZnO and TiO$_2$ (BET surface areas of 1.7 and 8.3 m^2/g); from Degussa, TiO$_2$ P25 (30 nm particle size and 50 ± 15 m^2/g 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 (Dionysiou *et al*., 2004). In the second set of experiments, a Pyrex® annular reactor containing 550 mL of wastewater was used, as shown in Fig. 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 at > 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 Fig. 1. All experiments were performed at 25 ± 1°C. The catalyst concentration ranged from 0.5 to 5.5 g/L 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.

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), and hydrogen peroxide concentration (5, 30, and 55 mmol/L). 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). 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 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. 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, Awwa, Wef, (1992).

RESULTS

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 (Kormann, *etal*., 1991). Control experiments in the dark showed no significant changes in the wastewater (Apha *etal*.,1992).

Another quite interesting finding is depicted in Fig. 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.

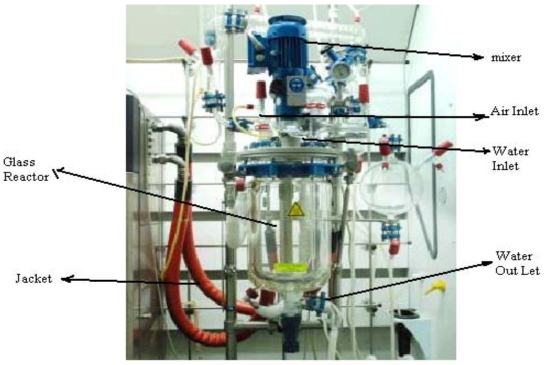


Fig.1: Buchi glass reactor used in this study

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, respectively. Those errors were quite a bit smaller than the values measured.

The response surfaces obtained are shown in Figs. 3,4. It can be seen that the highest degradations were achieved with the lower hydrogen peroxide concentration (5 mmol/L), which is in good agreement with the literature (Dionysiou *etal*., 2004) 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.

Regarding the UV area, it can be seen that the use of 3.0 g/L of TiO_2 resulted in a somewhat better degradation and that a pH close to 7 was the best one.

Table 2: The achieved results for phenol degradation for 60 min

Total phenol residual (%)	pH	$C_{photocatal}$ (g/L)	Catalyst	Degradation Enhancement
35.2	5.5	5.0	TiO2	
16.7	3.5	5.0	ZNO	
6.98	6.3	3.0	$TiO_2 P_{25}$	

* The parameter Degradation enhancement is compared to the efficiency obtained using the TIO2 supplied by Aldrich as the photo catalyst

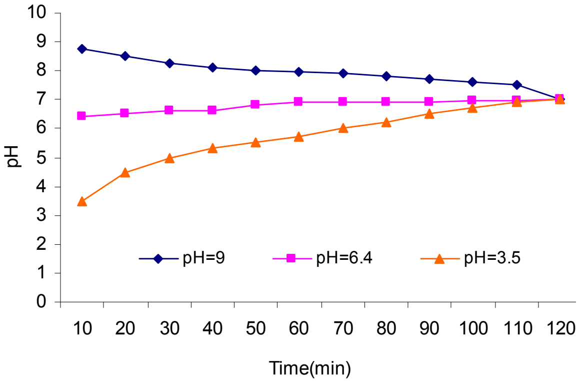


Fig.2: Evaluation of pH during photocatalysis (TiO_2: 3g/L) at different initial pHs

Table 3: Degradation (%) at the response surface

TiO_2 Conc.	Degradation (%) UV area	mg/L
0.5	73	83
3	79	81
5.5	71	93

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.

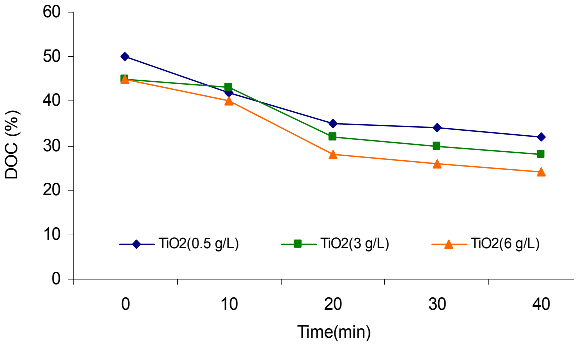
Therefore, the following experiments were performed using 3.0 g/L of TiO_2 and pH=6.3. Although this is not the best pH for phenol removal, it was estimated that degradation would decrease by only 10% with the neutral pH. It is noteworthy that the best experimental conditions obtained by the experimental design confirmed the ones found during the screening experiments.

Experiments under the optimized conditions

As it can be seen in Table 1, the COD/Dissolved oxygen Concentration ratio was approximately 10. In fact, this wastewater has a high content of sulfide, polisulfide, sulfonate, and chloride ions and ammonia. These 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 Fig. 5

Final Wastewater Characterization

After photocatalytically 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%).



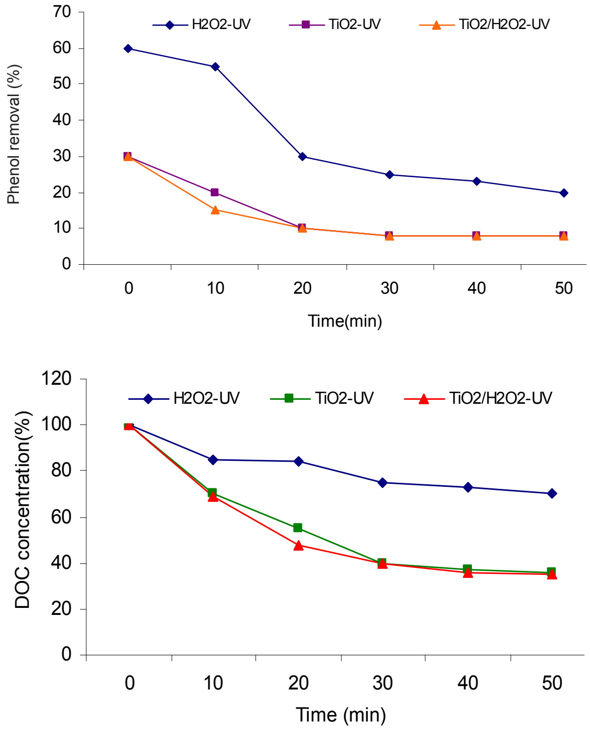


Fig. 3: Result for different oxidation processes under optimization conditions

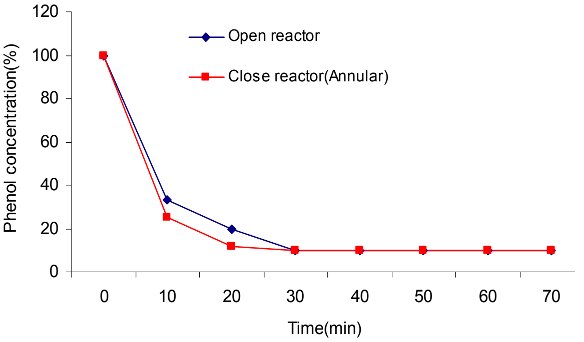


Fig. 4: The effect of concentration on the degradation process

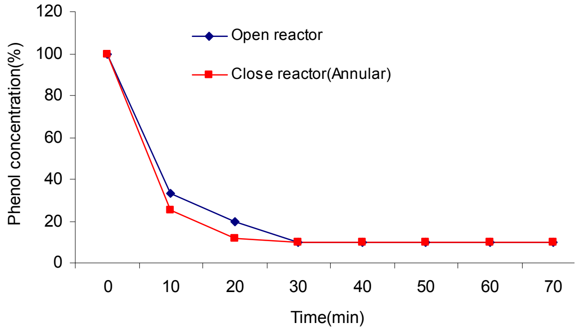


Fig. 5: Comparison between the performances of the reactors

Table 4: Wastewater photocatalytic treatment

TIO_2	Degradation% UV Area	Phenols,mgr/L
pH	6.7	7
DOC	20	10
Oil and grease	23	<10
Ammonia	70	50
Phenols	3.7	0.5

DISCUSSION

It was observed that the TiO_2 supplied by Aldrich was less active than the two others. This fact had already been reported elsewhere (Bessa *et al*., 1999). ZnO was twice as active, but its major drawback is 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 TiO_2 and ZnO supplied by Aldrich, respectively). Moreover, it offers two other advantages: less photocatalyst can be used (3 g/L compared to 5 g/L) 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 , is probably related to the nonpolar nature of the majority of the organic pollutants (alkanes) in the wastewater, although the concentration of alkanes was not measured (Tanaka *et al*., 1994). When the two sets of experiments are compared, it can be observed that performance of the Pyrex® annular reactor is better than that of the open The removal of phenols was quite the same, but DOC removal 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.

This wastewater showed insignificant changes when irradiated with UV light (proteolysis). 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_2O_2/UV, so the reactions that take place are much faster.

Moreover, the increase in degradation obtained by the use of H_2O_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 changed little after this time.

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).

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