

## Photocatalytic ozonation Removal from wastewater refinery with TiO<sub>2</sub> Nano-particles

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### Abstract

Wastewater treatment for water reuse is one of the main concerns in oil refineries since it can lead to high economic and environmental benefits. photocatalytic ozonation is a non-selective mineralization technology of organic matter in water by using active free radicals generated by ozone degradation. The COD removal was investigated by various advanced oxidation processes including UV, UV/TiO<sub>2</sub>, O<sub>3</sub>, O<sub>3</sub>/TiO<sub>2</sub>, O<sub>3</sub>/UV and UV/O<sub>3</sub>/TiO<sub>2</sub>. The obtained results revealed that all processes obeyed pseudo-first order kinetics and the coupled UV/O<sub>3</sub>/TiO<sub>2</sub> process was the most efficient method for the COD removal with high synergistic effect. The maximum COD removal efficiency during 60 minutes, to the process of reconciliation ozonation/photocatalysts average, about 84.16% respectively. Then, the effect of major operational parameters, such as ozone and TiO<sub>2</sub> dosage and pH on the efficiency of the significant coupled process was studied. changes in the initial 60 min of the processes taking place at the time of making, reduce slightly in pH resulting from the production of intermediates is created. Then by optimizing reaction conditions, it was found that most of the destruction in pH=11 done. Catalyst study showed different levels by increasing the amount of catalyst, the more contaminants are destroyed. Changes in the ozone rate, the removal efficiency of wastewater can make a large change, also showed the greatest changes in the initial 60 min of the processes taking place at the time of making, reduce slightly in pH resulting from the production of intermediates is created.

**Keywords:** Nano Titanium Dioxide, Refinery Wastewater, Advanced Oxidation Processes, Photo-catalysis, Photocatalytic Ozonation.

### Introduction

Today, due to industrialization, one of the biggest problems facing developed countries is the environmental pollution by hazardous chemicals [1]. Specifically, there is a growth in the amount of oil used in the industry, while the current technical and managerial developments for petroleum refinery wastewater treatment are not sufficiently efficient; Thus, a great amount of oil is discharged into the waters, causing hazardous pollution [2]. Impacts of petroleum refinery wastewater pollution include contamination of groundwater resources; drinking water; destruction of aquatic resources; atmospheric pollution; affecting agricultural production; endangerment of human health; and destruction of the natural environment [3]. Notably, petroleum refineries encompass intricate systems comprising various operations based on the specific type of crude being refined and the intended products. Due to various factors, it can be argued that each refinery exhibits unique characteristics, thereby rendering them distinct [4]. Furthermore, the composition of pollutants found in the effluent discharged from oil refineries is contingent upon the specific procedures undertaken during the refining operations. Hence, wastewater characteristics vary among refineries and can even differ within the same refinery based on the specific processes employed; besides, the difference in the type of pollutants in each unit in the refinery [5]. Alkanes, aromatics, and polycyclic hydrocarbons are major pollutants in refinery wastewater. Also, varying concentrations of ammonia, sulfide, phenols, and Benzo are generally present; in addition, the presence of other pollutants such as hydrogen sulfide (H<sub>2</sub>S), nitrogen, sulfur, and heavy metals that pose a threat to the environment due to their elevated toxicity and capacity to persist for prolonged durations [6]. Several methodologies were used to treat wastewater generated from refinery process involving single and hybrid approaches such as adsorption, coagulation and flotation, ultrasonically-dispersed nanoscale zero-valent iron particles, biological treatment, membrane filtration, and electrochemical coagulation. However, these methods have many drawbacks and being expensive or not efficient [7]. Recently, numerous approaches have been used for remediation various types of pollutants [8]. Advanced oxidation processes (AOPs), which can generate hydroxyl radicals (OH•), have been demonstrated to be a successful technique for the reduction of organic contaminants [9]. Titanium dioxide (TiO<sub>2</sub>) was recognized as an efficient photo-catalyst because it is active in the ultraviolet spectrum. Furthermore, in comparison with other materials used for water treatment such as CdS and ZnO, the application TiO<sub>2</sub> nanoparticles in the field of photo-catalysis has receiving more popularity due to increasing its surface area, easiness of preparation, having faster

rates with good biocompatibility non-toxic nature, and inexpensive [10]. The high disinfection and reactivity of ozone ( $O_3$ ), which is a stronger oxidant compared to oxygen ( $E^0=2.07$  V), makes it suitable for usage in water treatment processes [11]. Two possible routes in acidic or basic medium can occur for the degradation of organic contaminants, which are electrophilic reaction of ozone with them or  $O_3$  rapid decomposition to yield  $\cdot OH$  radicals, respectively [12]. However, it has been observed that complete degradation of pollutants may not be achieved by  $O_3$  process [13].  $TiO_2$ -catalyzed ozonation ( $O_3/TiO_2$ ) is more effective in comparison with ozone process alone for the degradation of humic and oxalic acid [14]. The enhanced degradation is due to the increase in ozone dissolution and decomposition in the presence of  $TiO_2$  particles [15]. The combination of UV with  $O_3$  is another technique used to degrade a wide variety of biorefractory and persistent contaminants in water more efficiently. The mechanical effects of UV lead to dissolving more ozone from the gas solution to the bulk solution because of the elimination of the mass transfer limitation and then more active radicals can be generated. In this study, refinery wastewater COD removal by using a combination of ozonation/photocatalysts were investigated.

## 2. Experimental

### 2.1. Materials

The laboratory experiments were performed using the pretreated refinery wastewater samples just at the inlet to the biological treatment unit in the Tabriz refinery plant. The chemical oxygen demand (COD), measured for this point, was within the range  $750 \text{ mg L}^{-1}$ . Titanium Dioxide ( $TiO_2$ ) Nano-particles (80% anatase and 20% rutile, with average particle size of 21 nm and surface area of  $50 \pm 15 \text{ m}^2/\text{g}$ ) was used as a photo-catalyst purchased from Degussa P25, Germany. All other chemicals were purchased from Merck, Germany.

### 2.2. Experimental set-up and procedure

Experiments were performed in a batch cylindrical quartz reactor with the inner diameter of 80 mm and the volume of 500 mL. The pH of the solution was adjusted by adding sodium hydroxide or perchloric acid. The glass cylinder was sealed with a polyethylene cap during operation. Ozone, which was supplied from the ozone generator (Donali, Iran), was fed to the reactor by a diffuser from its bottom. The concentration of ozone was adjusted by varying the power and measured by KI method. The experiments were performed in a temperature controlled bath. In each experiment, 250 mL of a reaction mixture was prepared. Then, the solution was treated by the chosen  $O_3$  dose and/or UV. Finally, the sample was analyzed for COD analysis.

### 2.3. Analytical methods

The chemical oxygen demand (COD) test is widely utilized as a precise method for determining the organic content of the wastewater. The test enables waste measurement based on the total quantity of oxygen needed to oxidize organic matters to carbon dioxide and water. In this investigation, COD was used as a response to evaluate the viability of the combined ( $O_3 + UV/TiO_2$ ) process for the degradation of organic contaminants in wastewater from petroleum refineries. 2 mL of effluent was digested with  $K_2Cr_2O_7$  as an oxidizing agent for 120 min at  $150^\circ\text{C}$  in a thermal reactor to ascertain COD value. After bringing the digested sample to ambient temperature, the COD concentration was measured using a spectrophotometer (MD200, Lovibond). The conductivity of solution was measured by a conductivity tester (HANNA Instrument Inc. Romania) while pH of solution was measured using a digital pH meter (ISOLAB Laborgerger GmbH, Germany).

## 3. Results and Discussion

### 3.1. Comparison of various AOPs for COD removal

The %COD remaining was calculated by the following equation.

$$\% \text{COD remaining} = 100 - ((\text{initialCOD} - \text{finalCOD}) / \text{initialCOD} * 100)$$

The individual effect of UV irradiation and  $TiO_2$  addition is negligible for COD removal. The decreasing order of %COD remaining by different AOPs processes after 60 min of treatment was  $TiO_2/UV/O_3$  (84.16%),  $UV/O_3$  (64.6%),  $TiO_2/O_3$  (58.7%),  $O_3$  (48.5%) and  $UV/TiO_2$  (12.7%).

The effects of experimental parameters including ozone and  $TiO_2$  dosage and pH on the COD removal were investigated.

By increasing the  $O_3$  dosage, the COD removal enhance due to formation of more oxidizing species like hydroxyl radicals. However, as can be seen from Fig. 1, more increase in  $O_3$  dosage do not have remarkable effect on %COD remaining because unreacted  $O_3$  being released in the system. The effect of  $TiO_2$  dosage on the %COD remaining was depicted.

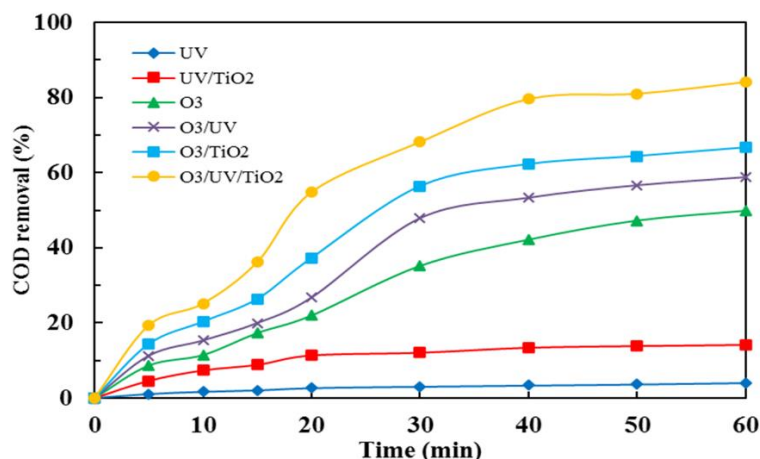


Figure 1. COD removal by different oxidation process, Experimental conditions: pH= 11, 250 mg/L TiO<sub>2</sub>, COD<sub>0</sub>= 750 mg/L, ozone gas concentration 10 mg/L.

### 3.2. The influence of experimental parameters on UV/O<sub>3</sub>/TiO<sub>2</sub> process

The effect of experimental parameters including ozone and TiO<sub>2</sub> dosage and pH on the degradation and mineralization of COD removal was studied. The %COD remaining was studied in the pH of 3, 7 and 11 (Fig. 2). With the increment of the solution pH from 3 to alkaline pH, overall COD abatement is enhanced for most wastewaters as expected. In general, ozone reacts with organic compounds found in water and wastewater via two different pathways namely direct molecular and indirect radical chain type reaction depending upon pH and composition of water [12]. It is expected that molecular ozone is the major oxidant at acidic pH, whereas less selective and faster radical oxidation (mainly hydroxyl radical) becomes dominant at pH > 7 as a consequence of OH• accelerated ozone decomposition [16]. Since the oxidation potential of hydroxyl radicals is much higher than that of ozone molecule, direct oxidation is slower than radical oxidation and furthermore, causes incomplete oxidation of organic compounds as observed in this study. However, low pH is known to suppress the formation of hydroxyl radicals from ozone and ozone is reacting directly by an electrophilic attack that led to 45 % lower COD removal than that obtained in the highest initial pH. In other words, at optimum values of the variables with the lowest initial pH, the COD removal achieved 39 %.

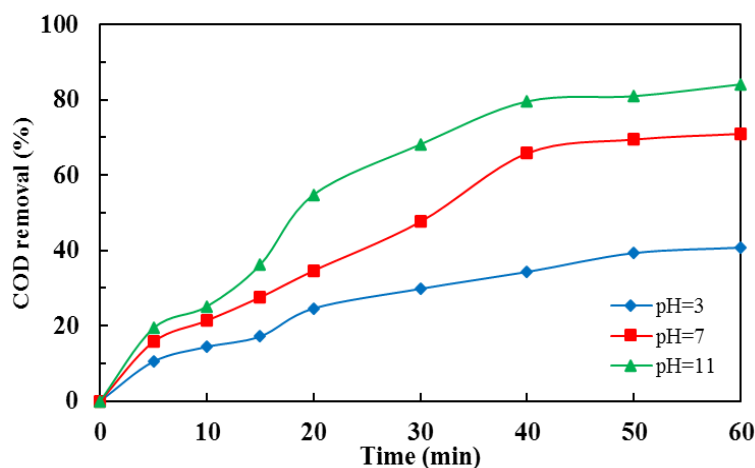


Figure 2. Effect of pH on COD removal, Experimental conditions: 250 mg/L TiO<sub>2</sub>, COD<sub>0</sub>= 750 mg/L, ozone gas concentration 10 mg/L.

The effect of TiO<sub>2</sub> dosage on the %COD remaining has been plotted in Fig. 3. Results illustrated the variation of COD removal. With catalyst concentrations up to about 300 mg L<sup>-1</sup>, the COD removal increases; while it decreases above this concentration during the same reaction. Similar behavior was observed for other times. Various reasons for this behavior have been offered without much conviction or quantification. A possible explanation is that increased turbidity of the solution reduces the light transmission through the solution, while below this level of concentration; it is assumed that the catalyst surface and the absorption of light by TiO<sub>2</sub> particles are limiting. Another case may be that of a near total light extinction which is occurred by catalyst particles at an optimum concentration [9]. The efficient

use of power and the optimization of catalyst concentration are key factors in achieving a satisfactory design in this regard.

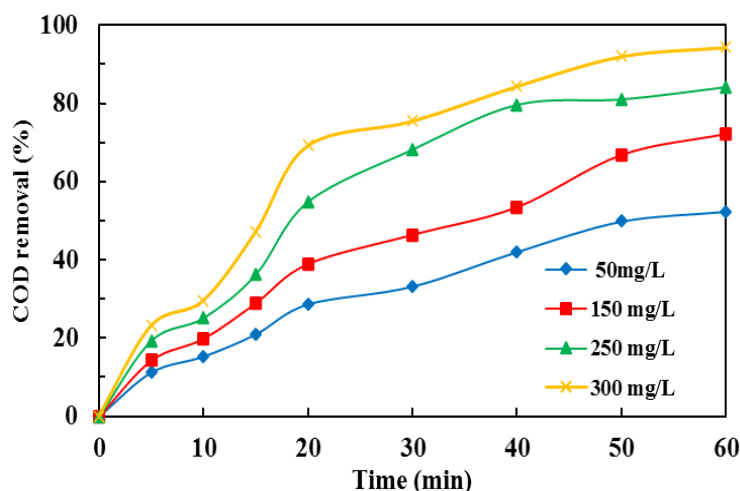


Figure 3. Effect of catalyst concentration on COD removal, Experimental conditions: pH=11, COD<sub>0</sub>= 750 mg/L, ozone gas concentration 10 mg/L.

By increasing the O<sub>3</sub> dosage, the COD removal were enhanced since the mass transfer of O<sub>3</sub> was improved and more oxidizing species like hydroxyl radicals were generated (Fig. 4) [17].

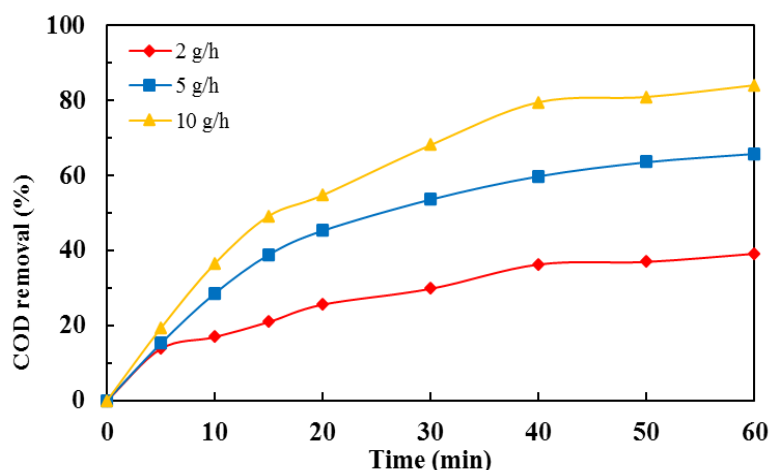


Figure 4. Effect of ozone dosage on COD removal, Experimental conditions: 250 mg/L TiO<sub>2</sub>, COD<sub>0</sub>= 750 mg/L, ozone gas concentration 10 mg/L.

## Conclusion

The COD removal was investigated via ozone, direct UV photocatalysis advanced oxidation processes with adding nano TiO<sub>2</sub>. The results of the present study have clearly delineated that using of ozone and UV with adding nano TiO<sub>2</sub> at alkalinity pH values provides a promising technique for COD removal of refinery wastewater. (Ozonation was demonstrated to be an effective method in increasing the COD removal). From the results, the oxidation rate is UV < (TiO<sub>2</sub>/UV) < O<sub>3</sub> < (O<sub>3</sub>/UV/ TiO<sub>2</sub>) and effect of TiO<sub>2</sub> on COD removal was obtained that by increasing TiO<sub>2</sub>, COD removal was increased. When UV irradiation was combined with nano TiO<sub>2</sub> and ozonation, the process performance in terms of COD removal efficiency increased significantly compared to that of single oxidants. The experiment with UV irradiation in neutral pH and experiment without UV irradiation had a significant COD removal in alkaline pH. The best result was obtained at pH 11 with 84.16 % COD removal efficiency. In the basis of the results obtained, the AOPs applied could be used as a pretreatment method prior a biological treatment process. And also, other advanced oxidation processes are recommended to be examined.

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## Nomenclature

COD: Chemical Oxygen demand

AOPs: Advanced oxidation processes

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