

## Degradation of 4-Nitrophenol from industrial wastewater by nano catalytic Ozonation

Aref Shokri\*

Young Researchers and Elite Club, Arak Branch, Islamic Azad University, Arak, Iran

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**ABSTRACT:** In this project, a nano catalyst ( $\text{TiO}_2$ ) and ozone combined with each other and they were used for the removal of 4-nitrophenol (4NP) in industrial wastewater. The effect of some operational parameters such as initial pH (3-9), the concentration of pollutant (20-80 mg/L), and amount of  $\text{TiO}_2$  were investigated. In  $\text{O}_3/\text{TiO}_2$  process, the anion radical ( $\text{O}^{\cdot-}$ ) formed before the production of hydroxyl radical. These results were different from the Ozonation process alone, in which high pH had a positive effect on the degradation of 4NP, because hydroxyl radicals was formed. In ozonation and  $\text{O}_3/\text{TiO}_2$  processes, about 89 and 97% of 4NP were degraded respectively, at optimum pH and 60 min of reaction. In catalytic ozonation the degradation rate of 4NP was higher at weak acidic pH conditions (pH=5). The removal of chemical oxygen demand (COD) was increased from 49% (only ozonation) to 74% ( $\text{O}_3/\text{TiO}_2$ ) at 90 min of reaction. The kinetic of degradation was pseudo-first-order and degradation and mineralization of 4NP were estimated by HPLC and COD tests, respectively.

**Keywords:** Chemical Oxygen demand (COD); Degradation; Industrial wastewater;  $\text{TiO}_2$  nano catalyst; 4-Nitrophenol (4NP)

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## INTRODUCTION

Industrial wastewater generated from Karoon petrochemical plant in Iran includes 4-Nitrophenol (4NP) and other aromatic derivatives. The chemical industries are considered to produce wastewater containing non-biodegradable and toxic compounds that remain in the environment even after their wastewaters have been subjected to conventional treatment [1]. Certain amounts of aromatic components are wasted during chemical processes which contains a wide range of non-biodegradable pollutants that cause environmental problems [2]. Nitro phenol is one of the most refractory compounds due to their high stability and solubility in water [3]. The classic methods of treatment have high operational costs, longer reaction time and

secondary pollution [4], so the use of advanced oxidation processes (AOPs) is inevitable.

AOPs produce very powerful and non-selective oxidizing agents such as hydroxyl radicals for degradation of refractory and hazardous pollutants in different wastewaters [5]. Ozone is a powerful oxidant and is used greatly in water treatment process [6-7]. But in most cases, it has been reported that ozone cannot degrade organic pollutants completely and sometimes generates toxic intermediates.

In these conditions, catalytic ozonation has been attracting the increasing notice as a result of its possibly higher efficiency and lower negative effect on water nature [8]. Supported and unsupported metals and metal oxides are the most commonly used catalysts for the ozonation of organic pollutants in water. Among various semiconductors, Titanium dioxide has been recurrently reported as an active,

\*Corresponding Author: Aref Shokri

Email: [aref.shokri3@gmail.com](mailto:aref.shokri3@gmail.com)

Tel.: (+98) 8633422211; Fax: (+98) 8633422217

inexpensive, and nontoxic semiconductor. It can accelerate the ozonation process for degradation of a wide range of different pollutants in recent years [9-13]. Although titania is mainly used in photo catalysis systems, also it has been proposed as an active catalyst in the ozonation of organic molecules [14]. In this work, degradation of 4NP as a industrial pollutant was studied by  $O_3/TiO_2$  process and the effect of pH on catalytic ozonation and the kinetic of reaction was investigated.

## EXPERIMENTAL

### Materials

4-Nitrophenol (4NP), NaOH and HCl (0.1M), sodium thiosulphate, and potassium iodide were of reagent grades and supplied from Merck, Germany. Titanium

dioxide (Degussa P-25, 70% Anatase and 30% Rutile, BET surface area of  $55m^2/g$  and an average particle size of 20 nm) obtained from Germany. The TEM and SEM pictures of the purchased  $TiO_2$  were presented in Figs. 1 and 2. Ozone was produced in an ozone generator that it was fed by dry oxygen. All reagents were used as received without further purification. Distilled water was used throughout this study.

### Apparatus

Experiments were performed in a semi batch (continuous for ozone and batch for  $TiO_2$  and 4NP) reactor. The pure oxygen, from a pressurized capsule, was entered into Ozone Generator (214V and 0.39A) from ARDA companies of Iran. The reactor was equipped with a water-flow jacket connected to a

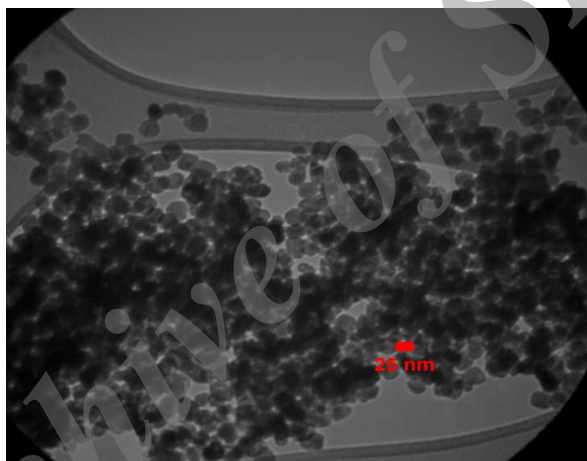


Fig. 1: TEM image of nano catalyst ( $TiO_2$ , Degussa P-25).

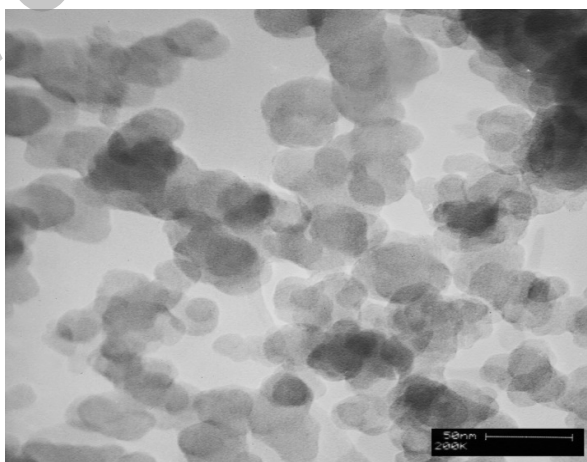


Fig. 2: SEM image of nano catalyst ( $TiO_2$ , Degussa P-25).

thermostat (BW20G model from Korean Company) for regulating temperature at 25°C which is shown in Fig. 3. The pH was adjusted by adding NaOH or HCl (0.1 M) and measured by pH Meter PT-10P Sartorius Instrument Germany. The progress in the degradation of 4NP was recorded by a high performance liquid chromatography (Knauer, Germany) equipped with Spectrophotometer (platm blue Germany). A reverse phase column filled with 3  $\mu\text{m}$  Separon C<sub>18</sub>, was 150 mm in length and 4.6 mm in diameter. PH was adjusted to 2.5 by Orthophosphoric acid and the Isocratic method was used by a solvent mixture of Acetonitrile and deionized water (60:40% v/v) with a flow rate of 1 ml/min at room temperature. In all tests, the suspension was centrifuged and filtered to collect the catalyst particles.

#### Catalytic ozonation tests

About 1000 ml of aqueous solution containing 40 mg l<sup>-1</sup> of 4NP and 1 gram of nano TiO<sub>2</sub> were mixed completely in the reactor. A mixture of O<sub>3</sub>/O<sub>2</sub> was produced by Ozone generator and entered from the bottom of the reactor by a porous diffuser for mixing well, saturating solution with O<sub>3</sub>, better mass transfer and reaction between ozone, TiO<sub>2</sub> and a pollutant. The concentration of gaseous ozone was measured by the iodometric method using 2% neutral buffered potassium iodide for ozone trapping and sodium thiosulfate as a titrant [15]. The flow rate of O<sub>3</sub>/O<sub>2</sub> mixture was kept constant at 0.5 Lmin<sup>-1</sup>, having an ozone concentration of 20.8 mg l<sup>-1</sup>. In order to know the amount of ozone consumed, the reactor outlet gas was bubbled through a KI (2%w) tamponed solution for determining unreacted ozone.

The producing iodine was titrated by standard Sodium thiosulphate in the presence of starch as an indicator. The amounts of not reacted and reacted ozone were determined and the value of ozone in tail gas was obtained, correspondingly. The residual of ozone in aqueous solution was estimated by a spectrophotometer using the Indigo method [16].

TiO<sub>2</sub> particles were dispersed and suspended in the solution as the ozone gas entered to the reactor. In all this project, the UV lamp above the reactor was off. Samples were withdrawn at different intervals and filtered to remove TiO<sub>2</sub> particles. The concentration of 4NP was determined by Spectrophotometric at 270 and 410 nm in acidic and alkaline media, respectively. The experiments were

carried out at pH in the range of 3-9. The wavelength of maximum absorption in the UV spectrum of 4NP was shifted at different pHs.

The HPLC methods were used for further validation and the two methods gave similar results. COD was measured by the standard closed reflux and Colorimetric method [17] and the absorbance of samples for COD was measured by spectrophotometer at 600 nm.

The removal of 4NP and COD as a function of reaction time is given by:

$$\text{Removal of 4NP(\%)} = \left( \frac{[4NP]_0 - [4NP]_t}{[4NP]_0} \right) \times 100 \quad (1)$$

$$\text{Removal of COD(\%)} = \left( \frac{[COD]_0 - [COD]_t}{[COD]_0} \right) \times 100 \quad (2)$$

Where [4NP]<sub>0</sub> and [COD]<sub>0</sub> are the concentration of 4NP and amount of COD at the start of the reaction, and [OT] and [COD] are the concentration of 4NP and amount of COD at time t, respectively.

## RESULTS AND DISCUSSION

### Effect of pH on Ozonation

The decomposition of ozone in aqueous solution depends on pH strongly, and it enhances with increase in pH [18]. The experiments carried out at pH values of 3, 5, 7 and 9 and as it can be seen from Fig. 4, the results showed that the removal efficiency raised from 45 to 89.3% in 60 min of reaction as the pH increased from 3 to 9 and the optimum pH during this process was 9 [19].

At pH=3, the formation of hydroxyl radicals was very low, so radical reactions happened slightly. The direct molecular ozonolysis were very predominant at acidic condition and ozone was reacted with pollutant directly and the double bonds of 4NP ring seem to be destroyed by ozonolysis. Whereas, hydroxyl radicals were strong oxidant originated from the reaction of hydroxide ions with ozone at high pH. Hydroxyl radicals initiated the chain oxidation reaction of ozone, which was non-selective and very fast [20].

### Effect of pH on TiO<sub>2</sub>/O<sub>3</sub> process

In TiO<sub>2</sub>/O<sub>3</sub> system, pH has two direct impacts on the process, one is ozone disintegration and the other one is surface charge and characteristic of TiO<sub>2</sub> nano

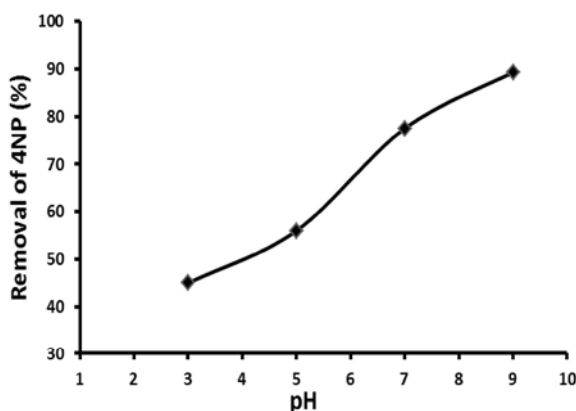


Fig. 3: Effect of pH on ozonation of 4NP ( $[O_3]_0 = 20.8 \text{ mg L}^{-1}$ ,  $[4NP]_0 = 40 \text{ mg L}^{-1}$ ).

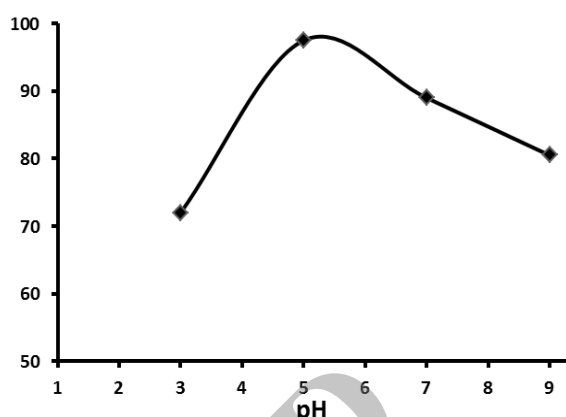


Fig. 4: Effect of pH on  $TiO_2/O_3$  process ( $[TiO_2] = 1 \text{ g L}^{-1}$ ,  $[O_3]_0 = 20.8 \text{ mg L}^{-1}$ ,  $[4NP]_0 = 40 \text{ mg L}^{-1}$ ).

catalyst which has a direct influence on their adsorption ability towards the molecules of pollutant [21, 22]. The point of zero charge (PZC) of the  $TiO_2$  was reported at 6.6 [23] and this factor affects the adsorption of pollutant on catalyst and it was determined by Potentiometric titration as explained by Halter [24]. Organic pollutants in neutral state

may adsorb on the surface of catalyst if the surface is not charged near the  $pH_{PZC}$  of the catalyst [25].

The effect of pH on  $TiO_2/O_3$  process is shown in Fig. 5. From the experimental results, it was clear that the best results were obtained at a slightly acidic pH. After 60 min, the degradation efficiency of 4NP was 97% in weak acidic condition ( $pH = 5$ ), while in the solutions with pH 3, 7 and 9 it was about 72, 89 and 80.5%, respectively. The surface features and the electrostatic interactions between  $TiO_2$  and hydroxide ions in the solution were the main factors affecting the degradation of pollutant.

#### **Decomposition of 4NP with $TiO_2/O_3$ and $O_3$ processes**

There is still a considerable shortage of knowledge related to the role of metal oxides in the ozonation process, especially with relation to the ozone decomposition reaction. It has been suggested that ozone can be adsorbed on a catalyst surface to yield different oxidizing species [26]. The proposed mechanism mentioned that ozone and organic molecules adsorbed on the catalyst surface concurrently, ozone degrades on the metallic sites and produce the surface bond radical ( $O^{\bullet-}$ ) that they are

more reactive than ozone and lead to the oxidation of adsorbed organic pollutants by near  $O^{\bullet-}$  radical. Oxidation advances through some oxidized intermediates gradually, while radicals are continuously produced by dissolving ozone that is transferred to the catalyst surface. The attraction of the oxidation products to the surface of catalyst reduces and final degradation products repulse from the catalyst surface [27].

As it can be seen from Fig. 6, experiments were performed in 90 min for comparative study of different processes in their optimum pH. Only 6% of 4NP disappeared when contacted with  $TiO_2$  alone at  $pH = 5$ , because pollutant adsorbed on the surface of nano catalyst. In runs with  $TiO_2/O_3$  and  $O_3$  processes, 97 and 89% of 4NP was removed, respectively. The corresponding results indicated that the presence of  $TiO_2$  can accelerate the degradation of 4NP rather than the ozone oxidation alone. In addition, the  $TiO_2$  has the ability to enhance the decomposition of ozone and promote the formation of hydroxyl radicals. According to preliminary experiments, about  $1 \text{ g L}^{-1}$  of  $TiO_2$  was used because it can initiate the degradation of 4NP and at high dosage of catalysts the aggregation of  $TiO_2$  particles happens.

#### **Effect of initial concentration of 4NP on the removal efficiency**

The effect of initial concentration of 4NP on the efficiency of degradation in  $TiO_2/O_3$  was investigated over the concentration range from 20 to 80 mg/L and results showed in Fig. 7. Results revealed that the rate of removal was reduced with increase in the initial

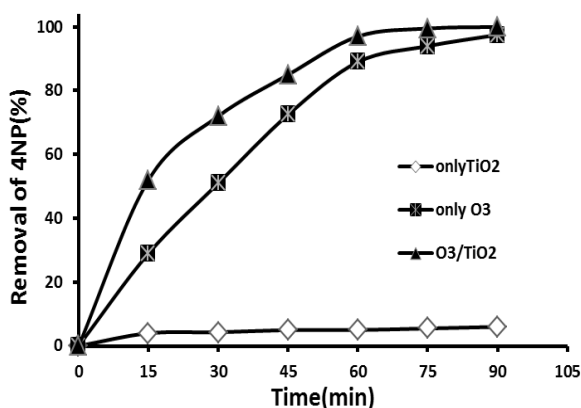


Fig. 5: Degradation of 4NP during Ozonation and catalytic ozonation process (optimum pH for each process,  $[\text{TiO}_2] = 1 \text{ g L}^{-1}$ ,  $[\text{O}_3]_0 = 20.8 \text{ mg L}^{-1}$ ,  $[\text{4NP}]_0 = 40 \text{ mg L}^{-1}$ ).

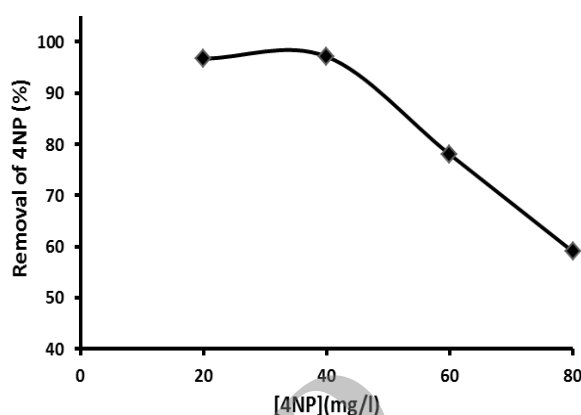


Fig. 6: The effect of initial concentration of 4NP on the efficiency of  $\text{TiO}_2/\text{O}_3$  process (pH=5,  $[\text{TiO}_2] = 1 \text{ g/l}$ , time = 60 min).

concentration of 4NP. When the initial dosage of the pollutant was high (80 mg/L), the number of available active sites and the generation of hydroxyl radicals decreased by 4NP molecules, because of their competitive adsorption on  $\text{TiO}_2$  surface, and only 59% of the pollutant degraded after 90 min of reaction [28]. With an increase in the initial concentration of 4NP, active agents such as hydroxyl radicals originated from the process decreased because they react with a large number of pollutant molecules [29]. When the concentration of 2NP increased, the surface of  $\text{TiO}_2$  was covered by pollutant molecules instead of ozone and production of active agents for destroying pollutant decreased subsequently. But, if the number of pollutant molecules is very low, their collision with active sites were low and degradation efficiency decreased.

#### Reusability of the nano catalyst

The reusability of the  $\text{TiO}_2$  catalyst was investigated for degradation of 4NP. The  $\text{TiO}_2$  particles were separated from the solution by filtration, then washed with distilled water and regenerated by drying and heating at  $150^\circ\text{C}$  for two hours. At high temperature the adsorbed molecules on the surface was removed and some of the active sites were released.

An equal amount of regenerated catalyst was used for the degradation of 4NP in optimum experimental condition. After three runs of the experiment, the degradation efficiency decreased to 94, 83 and 69%. The following descriptions are the reason of this falling efficiency: (I) adsorption of intermediates and side product of the process in the active sites and on

the surface of the catalyst lead to decrease in degradation efficiency [30], (II) titanium ions were transferred to the solution and the active sites on the catalyst surface removed, so the activity of the remained catalyst decreased, (III) the structure and morphology of catalyst matrix deformed gradually by continuous heating in the regeneration process. It was clear that using ozone along with  $\text{TiO}_2$  prevents from catalyst deactivation [31]. The removal efficiency of COD was studied by  $\text{O}_3$  and  $\text{O}_3/\text{TiO}_2$  processes in optimum pH obtained for degradation of each process. The removal of COD through the degradation of 4NP is shown in Fig. 8.

In  $\text{O}_3/\text{TiO}_2$  process, about  $1 \text{ g L}^{-1}$  of catalyst was added to the solution and amounts of COD decreased sharply during the first 30 min and then decreased slowly. After 90 min of treatment, the removal of COD was 49 and 74% in  $\text{O}_3$  and  $\text{O}_3/\text{TiO}_2$  process, respectively. It is clear that ozonation alone is a slow process, but the  $\text{O}_3/\text{TiO}_2$  is a rapid one. So, it can be inferred that 4NP was mineralized partially and some degradation intermediates were created during the process [19] and 4NP cannot be totally mineralized even by the  $\text{O}_3/\text{TiO}_2$  methods.

By destroying the structure of 4NP in the process, the nitro groups from the aromatic ring was converted to nitrate and these ions generated from the beginning of the treatment [32].

#### Kinetic study of degradation of 4NP with $\text{O}_3/\text{nano-TiO}_2$ process

A kinetic study for degradation of 4NP in  $\text{O}_3/\text{TiO}_2$  process was performed at optimum pH (pH= 5). The

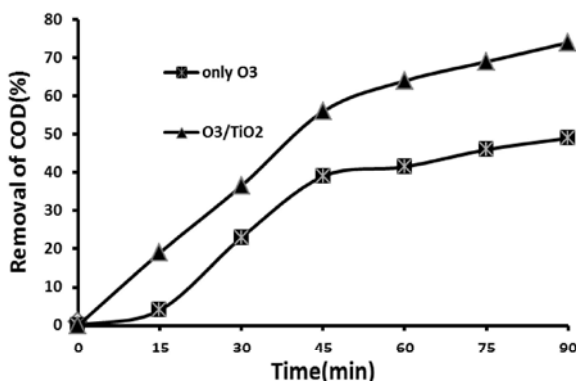


Fig. 7: Removal of COD in ozonation and catalytic ozonation of 4NP during 90 min (pH =9 in  $O_3$  and pH =5 in  $O_3/TiO_2$  process,  $[TiO_2] = 1 \text{ g L}^{-1}$ ,  $[O_3]_0 = 20.8 \text{ mg L}^{-1}$ ,  $[4NP]_0 = 40 \text{ mg L}^{-1}$ ).

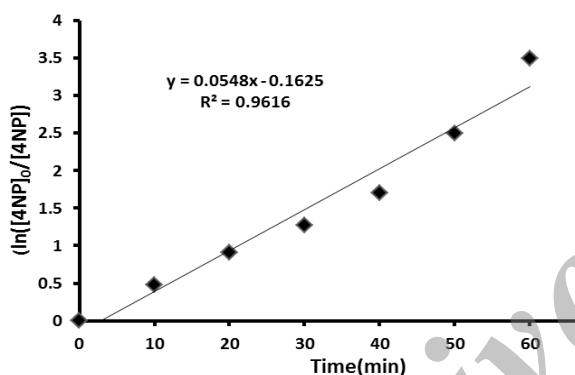


Fig. 8: The curve of  $\ln \frac{[4NP]_0}{[4NP]_t}$  versus reaction time in  $O_3/TiO_2$  process (pH = 5,  $[TiO_2] = 1 \text{ g L}^{-1}$ ,  $[O_3] = 20.8 \text{ mg L}^{-1}$  and  $[4NP]_0 = 40 \text{ mg L}^{-1}$ ).

kinetic relation for degradation of 4NP by the mentioned process can be introduced as:

$$\frac{-d[4NP]}{dt} = k_{O_3}[4NP][TiO_2][O_3] + k_{OH^\bullet}[4NP][TiO_2][OH^\bullet] \quad (3)$$

Where  $[4NP]$ ,  $[O_3]$ ,  $[OH^\bullet]$  and  $[TiO_2]$  are the concentrations of 4NP, ozone, hydroxyl radicals and  $TiO_2$ , respectively. Moreover  $k_{OH^\bullet}$  and  $k_{O_3}$  are the rate constants of 4NP with hydroxyl radicals and ozone. At low pHs, the selective reactions of molecular ozone with 4NP were superior [32], so the kinetic equation can be written as:

$$\frac{-d[4NP]}{dt} = k_{O_3}[4NP][TiO_2][O_3] \quad (4)$$

In this process, 4NP was degraded by reaction with  $TiO_2$  and  $O_3$  and the ratio of the concentration of 4NP to  $O_3$  or  $TiO_2$  was low, so the concentration of  $O_3$  and catalyst can be considered constant. In these conditions only the concentration of 4NP was changed and the reaction can supposed to be pseudo-first-order [33]. So, the equation rate can be shown as:

$$\frac{-d[4NP]}{dt} = k'_{O_3}[4NP] \quad (5)$$

Where,  $k'_{O_3}$  is a pseudo first-order rate reaction of 4NP with  $O_3/nano-TiO_2$ . The integration from Eq. (5) produced the following equation:

$$-\ln \frac{[4NP]}{[4NP]_0} = k'_{O_3} t \quad (6)$$

Where  $[4NP]$  and  $[4NP]_0$  are the concentration of 4NP in time =t and time=0, respectively. As it can be seen from Fig. 8, the term  $\ln \frac{[4NP]_0}{[4NP]_t}$  versus reaction time was plotted and after linear regression analysis, the apparent first order rate constants ( $k'_{O_3} = 54.8 \times 10^{-3} \text{ min}^{-1}$ ) and half-life of degradation reaction ( $t_{1/2} = 12.6 \text{ min}$ ) were determined (Eq.6).

## CONCLUSION

The combination of ozone and  $TiO_2$  catalyst had more effect on the removal of 4NP in aqueous solutions and based on the experimental results the following conclusions were obtained:

The decomposition of ozone was accelerated by the nano catalyst of  $TiO_2$  under partly acidic conditions (pH=5). In  $TiO_2/O_3$  system, the pH had two direct effects on the process, one was ozone decomposition and the other one, surface charge and characteristic of  $TiO_2$  nano catalyst. The degradation efficiency of 4NP was higher at slightly lower pH than high pH (pH =9).

The removal percent of 4NP was 97 and 89% at 60 min of reaction, also the removal of COD was 74 and 49% after 90 min of treatment in  $TiO_2/O_3$  and  $O_3$  processes, respectively. The adsorption and following reaction of 4NP on  $TiO_2$  sites was responsible for the improvement of ozonation rate observed in catalytic runs. From the kinetic study, it was clear that in  $O_3/TiO_2$  process the equation rate for degradation of 4NP was pseudo-first-order and after linear regression,  $R^2$

obtained at 0.9616. A little deviation from 1, was because of assuming this concept that hydroxyl radical reactions were negligible in slightly acidic conditions.

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