Degradation of Terphetalic Acid from Petrochemical Wastewater by Ozonation and O₃/ZnO Processes in Semi Batch Reactor

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Background & Aims of the Study: One of the toxic pollutants in the wastewater of petrochemical industries is Terphetalic acid. In this study, the degradation and mineralization of Terphetalic acid in aqueous environment were studied by Ozonation and O₃/ZnO processes in a semi batch reactor.

Materials & Methods: This study is an experimental research on a laboratory scale. The study executed on synthetic wastewater having Terphetalic acid. The impact of operational factors such as pH, initial concentration of ZnO and Terphetalic acid was also studied.

Results: Different amounts of variables were optimized for the removal of Terphetalic acid in O₃/ZnO process. The optimum conditions were achieved as follows: the [ZnO]=1.20 g/l, pH at 9, and [TPA]=70 mg/l.

Conclusions: The results exhibited that at the predicted optimum conditions and after 30 min of reaction, the removal of Terphetalic acid and Total Organic Carbon (TOC) was 96.9 and 44.3%, respectively. The O₃/ZnO process was powerful in the removal of TPA, but it can remove the TOC to some extent.

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Background

Terephthalic acid (TPA) is commonly employed as a raw material for different petrochemical products such as polyethylene terephthalate, polyester films, bottles, and textile fibres. Also, it has been used as an additive to produce medicines, dyes, synthetic perfumes, pesticides, and other chemical compounds. The TPA and its esters are doubted to cause cancer, urinary bladder, tumor promoters, endocrine disruption and renal damage (1). Thus, wastewater that holds these pollutants must be remediated before being discharged into the environment.

Some techniques were used for the TPA removal such as coagulation–flocculation (2) that the contaminant is only transferred to another phase, photocatalysis (3) and supercritical water oxidation (4). The photocatalysis can be very slow, and it has not been able to remove TPA absolutely. The supercritical water oxidation needs equipment, which works under high temperature and pressure. The classic remediation methods have great operating costs, extended treatment time and secondary contamination (5), therefore
using advanced oxidation processes (AOPs) is necessary. AOPs comprise the generation of hydroxyl radicals, for the removal of recalcitrant pollutants in various wastewaters (6). Ozone is a dominant oxidant and is employed significantly in the remediation of wastewater process (7). But, the resistant organic pollutants are usually not completely oxidized and only a small mineralization is attained. Furthermore, the practical use of ozonation for wastewater treatment is limited by its high-energy request.

Some methods have been used to improve the oxidizing power of ozone and reducing the required reaction time and energy cost. The mixture of solid catalysts with ozone has recently confirmed interesting capacities for the oxidation of industrial wastewater and surface waters, and removal of pollutants in aqueous solutions. Heterogeneous catalytic ozonation is a novel type of AOPs which combines ozone with the solid-phase metal oxide catalysts at room temperature for mineralization of organic contaminants (8). Zinc oxide (ZnO) is a cheap and famous catalytic material that is used as a heterogeneous catalyst, with a high catalytic activity, non-toxic, and insoluble (9).

The influence of ZnO on ozone disintegration to generate hydroxyl radicals was not clear. Some researcher recommended mechanisms based on non-radical system that form hydroxyl radical. Some mechanisms are offered, but the direct production of hydroxyl radicals from ozone degradation on the surface of ZnO or indirect generation as a result of inferior reactions was still unidentified (10). Some researchers (11-12) have stated that the adsorption and the subsequent reaction of pollutants on catalyst sites are in charge of the enhancement of catalytic ozonation.

Based on the researches of many investigators, there is still a considerable absence of information related to the role of ZnO in ozonation process (10).

**Aims of the study:**

In this study, degradation of TPA as an aromatic pollutant was investigated by O$_3$/ZnO process and the effect of pH, initial concentration of TPA and amount of ZnO for higher degradation of TPA was investigated. Also, a kinetic study was developed using the experimental results attained in this study.

**Materials & Methods**

**Material**

Terephthalic acid was supplied from HIMEDIA. Potassium iodide, HCl and NaOH, and sodium thiosulphate were supplied from Merck. All the chemicals used in the study were of analytical reagent (AR) grade. Different concentration of terephthalic acid was used to prepare synthetic solutions. Zinc oxide was purchased from Degussa, Germany. Distilled water was used during this study. All substances were employed as received without further purification.

**Photo reactor**

The experiments were performed in a semi batch (continuous for ozone and batch for ZnO and TPA) reactor. The pure oxygen, from a pressurized capsule, was passing in Ozone generator from ARDA companies of Iran. The reactor was prepared with a water-flow jacket joined to a thermostat (BW20G model, Korean Company) for regulating temperature at 25ºC in all tests (Fig.1). The advancement in the degradation of the TPA was logged by a high performance liquid chromatography (HPLC). A reverse phase column was packed with 3 μm Separon C$_{18}$ with 150 mm in length and 4.6 mm in width. An isocratic mode was used with attuned pH to 2.5, by orthophosphoric acid and a solvent blend of acetonitrile and deionized water (60:40% v/v) at a flow rate of 1 ml/min at room temperature. In all experiments, the suspension was centrifuged and filtered to separate the catalyst particles. The pH was measured by pH Meter PT-10P Sartorius Instrument Germany.
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Figure 1) Schematic diagram of the experimental set-up.

Notes: 1- Pure oxygen, 2- Needle valve, 3- Rota meter, 4- Ozone generator, 5- Washing bottle, 6- Reactor, 7- Magnetic stirrer, 8- Ozone diffuser, 9- Magnetic bar, 10- Sampling system, 11- Cooling water return to thermostat 12- Cooling water supply from thermostat.

General procedure
About 1500 ml of aqueous solution having definite concentration of the TPA and nano ZnO were mixed appropriately in the reactor. A mixture of O3/O2 was created by Ozone generator and entered from the bottom of the reactor by a spongy diffuser. The concentration of ozone in gas phase was estimated by the iodometric method employing 2% neutral buffered potassium iodide for ozone trapping and sodium thiosulfate as a titrant (13). The concentration of ozone was kept at 8.6 mg L⁻¹.

ZnO particles were spreaded in the reactor by the entering ozone gas. Samples were withdrawn at different intervals and the concentration of TPA was measured by Spectrophotometric at 240 nm. The HPLC and spectrophotometry methods presented similar results and the difference between them was little. The tests were executed in the pH range of 3-11. The pH was regulated only at the start of the reaction using NaOH (0.1 M) and HCl (0.1 M).

Total organic carbon (TOC) was checked with a Shimadzu TOC-VCSN provided with an automatic auto sampler and platinum based catalyst. The carrier gas was synthetic air at the rate of 0.15 L min⁻¹. Before the samples being sent to TOC analyzer, the pH was acidified to lower than 4 to make certain that inorganic carbon would be released as CO₂ from the solution (14). The removal percent of TPA and TOC is introduced by the resulting equations (Eqs.1–2):

Removal of TPA (%) = \( \frac{[\text{TPA}]_0 - [\text{TPA}]}{[\text{TPA}]_0} \times 100 \)  \hspace{1cm} (1)

Removal of TOC (%) = \( \frac{[\text{TOC}]_0 - [\text{TOC}]}{[\text{TOC}]_0} \times 100 \)  \hspace{1cm} (2)

Where [TPA]₀ and [TOC]₀ are the initial concentrations of TPA and TOC at the beginning of the reaction, and [TPA] and [TOC] are the concentration of the TPA and extent of TOC at time t, respectively.

Results
Influence of pH on Ozonation
The decomposition of ozone in aqueous environment depends on pH intensely, and it improves with rise in pH (14). The tests were performed at pH values of 3, 5, 7, 9 and 11 and as it was presented in Fig. 2, the results revealed that the removal efficiency upraised from 49.5 to 89.5% at 30 min of reaction as the pH improved from 3 to 9 and then reduced to 83.5%. Therefore, the optimal pH in ozonation process was 9.

Influence of catalyst amounts on ZnO/O3 process
The influence of catalyst amount on the degradation of TPA is showed in Fig. 3. In the...
ozonation process, the action of free radicals produced from self-decomposition of ozone was minor; therefore the ordinary conversion of the TPA was attained. It is satisfactory that the hydroxyl radicals were produced by the fragmentation of ozone (15). But as represented in Fig. 3, the degradation efficiency was improved from 82.5 to 92.6% by the rise in catalyst dosage from 0.4 to 1.2 g L⁻¹. A more increase in catalyst amounts to 1.6 g L⁻¹ did not yield any notable increase in the removal efficiency. The dissimilarity between the removal efficiency of TPA at 1.2 and 1.6 g L⁻¹ of ZnO was insignificant, therefore 1.2 g L⁻¹ of catalyst was achieved as an finest concentration of ZnO from an economic view and other tests were made in this concentration of ZnO.

Figure 3) The influence of ZnO amounts on the removal of TPA in ZnO/O₃ process ([O₃]₀=8.6 mg L⁻¹, [TPA]₀= 70 mg L⁻¹, pH=7, time =30 min).

Effect of pH on ZnO/O₃ process

The influence of pH on ZnO/O₃ process is revealed in Fig.4. It was obvious that the finest results were gained at pH=9. After 30 min, the degradation efficiency of TPA was 96.9% in alkaline condition (pH=9), whereas in the solutions with pH 3,5,7 and 11 it was about 52.2, 71.5, 92.6, and 88.8%, respectively. The surface characteristics and the electrostatic contacts among ZnO and hydroxide ions in the aqueous phase were the important aspects distressing the removal of TPA.

Figure 4) Influence of pH on ZnO/O₃ process ([ZnO] = 1.2 g L⁻¹, [O₃]₀= 8.6 mg L⁻¹, [TPA]₀=70 mg L⁻¹, time =30 min).

Influence of initial concentration of TPA on the degradation efficiency

The influence of initial concentration of TPA in ZnO/O₃ process was studied at a range from 50 to 110 mg/l and results showed in Fig.5. The removal efficiency was improved a little from 96 to 96.9% by an enhancement of TPA dosages from 50 to 70 mg/l, but the removal efficiency of the TPA was reduced to 49.3% by an increase in its initial concentration from 70 to 110 mg/l. At high concentration of TPA (110 mg/l), the TPA molecules were adsorbed on active sites of ZnO and the formation of hydroxyl radicals was decreased.

Figure 5) Influence of initial concentration of TPA on the removal efficiency in ZnO/O₃ process (pH=9, [ZnO] =1.2 g L⁻¹, time=30 min).

Degradation of TPA by ZnO/O₃ and O₃ processes

For comparative study of various processes in their optimal pH, the experiments were performed at 60 min of reaction. About 5% of TPA was disappeared in ZnO alone at pH of 9, because of the adsorption of TPA molecules on the surface of ZnO at a dosage of 1.2 g L⁻¹. In
runs with ZnO/O₃ and O₃ processes, 96.9 and 89.6% of TPA was degraded, respectively. Consequently, the TPA removal efficiency in the ZnO/O₃ was higher than the sum of the separate effects of single adsorption and only ozonation.

The results were revealed that the presence of ZnO can quicken the degradation of TPA rather than the ozone oxidation alone. In addition, the ZnO has the ability to improve the decay of ozone and encourage the formation of hydroxyl radicals.

![Figure 6) Removal of TPA in ZnO/O₃ and O₃ processes ([TPA]₀= 70 mg L⁻¹, [O₃]= 8.6 mg L⁻¹, pH at 9, [ZnO] =1.2 g L⁻¹)](image)

The removal efficiency of TOC was studied in O₃ and O₃/ZnO processes in optimum condition and after 30 min of treatment, in O₃ and O₃/ZnO process, the removal of TOC was 31.5 and 44.3%, respectively. It is obvious that single Ozonation is a slow method, but the O₃/ZnO is a better to some extent. So, it can be inferred that TPA was mineralized incompletely and some degradation intermediates were formed in the process and TPA cannot be totally mineralized even by the O₃/ZnO process at 30 min of reaction and it needs more times (16).

Kinetic study in degradation of TPA by O₃/ZnO process

According to the mentioned studies, it is clear that the possible mechanism for the O₃/ZnO process included an indirect reaction through hydroxyl radicals and a direct reaction after the ozone and TPA adsorbed on the surface of ZnO. The kinetic equation for the removal of TPA by the introduced process can be as the following:

$$\frac{-d[TPA]}{dt} = k_{O3}[TPA][O_3] + k_{OH}[TPA][ZnO][OH^\cdot]$$  \hspace{1cm} (3)

Where [TPA], [O₃], [OH^\cdot] and [ZnO] are the concentrations of TPA, ozone, hydroxyl radicals and ZnO, respectively. Furthermore, $k_{OH^\cdot}$ and $k_{O3}$ are the rate constants of TPA with hydroxyl radicals and ozone. At pH of 9, the non-selective reactions of hydroxyl radicals with TPA were important, thus the kinetic relation can be presented as:

$$\frac{-d[TPA]}{dt} = k_{OH^\cdot}[TPA][ZnO][OH^\cdot]$$  \hspace{1cm} (4)

In these conditions only the concentration of the TPA was altered and the reaction can supposed to be pseudo-first -order. So, the equation rate can be written as:

$$\frac{-d[TPA]}{dt} = k_{OH^\cdot}[TPA]$$  \hspace{1cm} (5)

Where, $k_{OH^\cdot}$ is a pseudo first-order rate reaction of TPA with hydroxyl radicals produced from O₃/nano- ZnO process. The integration of Eq. (5) results in:

$$-\ln \frac{[TPA]}{[TPA]₀} = k_{OH^\cdot}t$$  \hspace{1cm} (6)

Where $[OT]$ and $[OT]₀$ are the concentration of OT in time $t$ and time=0, respectively. As it can be seen from Fig.7, the term $\ln \frac{[TPA]}{[TPA]₀}$ versus reaction time was designed and the apparent first order rate constants ($k_{OH^\cdot} = 111.2 \times 10^{-3} min^{-1}$)and half-life of reaction ($t_{1/2} = 6.25 min$) were determined (Eq.6).
Discussion

In only ozonation process and at pH=3, the creation of hydroxyl radicals was very low, so radical reactions happened somewhat, but direct molecular ozonolysis were very significant and ozone was reacted with TPA directly and the double bonds of TPA ring demolished by ozone. However, hydroxyl radicals were robust oxidant created from the reaction of hydroxide ions with ozone at alkaline pH and it was started the chain oxidation reaction of ozone, which was non-selective and very fast. At pH=11, radical scavenging has happened because of more hydroxide ion and accordingly more hydroxyl radicals manufacture (17).

The degradation efficiency of the TPA was expressively improved in the presence of both ozone and catalyst. An special characteristic of nano ZnO is its really high surface area. It is clear that the degradation of the TPA was according to the action of some ozone absorbed species or free radicals formed possibly on the catalyst surface or in the aqueous solution. Catalyst amounts had a positive effect on TPA removal in ZnO/O3 process.

In ZnO/O3 system pH had two direct influences on the process, one is ozone disintegration and the other one is surface charge and properties of ZnO nano catalyst which has a direct effect on their adsorption of pollutant molecules (18).

The point of zero charge (PZC) of the ZnO is reported in 9.0 (19). Organic contaminants in neutral state can be adsorbed on the surface of ZnO if the surface is not charged near the PZC (20).

It has been proposed that ozone can be adsorbed on a catalyst surface to produce various oxidizing types (21). The proposed mechanism mentioned that ozone and TPA were adsorbed on the catalyst surface simultaneously, ozone degrades on the metallic sites and produce the surface bond radical (O2) that they are more active than ozone and lead to the creation of hydroxyl radicals. Oxidation lasts through some oxidized intermediates progressively, while O2 radicals are continuously formed by dissolving ozone that is shifted to the catalyst surface. The absorption of the oxidation products to the surface of catalyst decreases and final degradation products reject from the catalyst surface (22).

At high concentration of TPA, active agents such as hydroxyl radicals initiated from the process were reduced because they react with a large number of pollutant molecules (23). When the concentration of TPA enlarged, the surface of ZnO was covered by pollutant molecules instead of ozone and following creation of active agents for degradation of pollutant reduced. However, when the number of pollutant molecules was very low, their impacts with active sites were diminished and degradation efficiency decreased (24).

Conclusion

According to the experimental results the following conclusions are achieved:

The nano catalyst of ZnO quickens the disintegration of ozone under alkaline condition (pH=9). In ZnO/O3 system, the pH has two direct influences on the process, one is ozone decomposition and the other one is surface charge and characteristic of ZnO nano catalyst. The removal of TPA is 96.9 and 89.6% at 30
min of reaction; also the removal of TOC is 44.3 and 31.5% after 30 min of reaction in ZnO/O_3 and O_3 processes, respectively. The adsorption and the next reaction of TPA on ZnO sites are responsible for the high removal rate of TPA in O_3/ZnO process. From kinetic studies, it is obvious that in O_3/ ZnO process the rate equation for degradation of the TPA is pseudo-first-order and after linear regression analysis, R^2 is acquired at 0.9077 and a deviation from 1, is because of supposing this phenomena that direct and selective reactions of ozone are insignificant in the experimental conditions.

### Footnotes

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**Conflict of Interest:**

The authors declared no conflict of interest.

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