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Degradation of Ortho-Toluidine in petrochemical wastewater by ozonation, UV/O_3, O_3/H_2O_2 and UV/O_3/H_2O_2 processes

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ABSTRACT

In this research, degradation of Ortho-Toluidine (OT) that is considered toxic and carcinogenic in the wastewater of petrochemical industries was investigated by advanced oxidation processes in circulating photoreactor. The effect of some operational parameters such as pH, flow rates of ozone, dosage of the OT, and concentration of hydrogen peroxide pollutant was investigated. The degradation and relative mineralization of the OT were estimated by HPLC and COD tests, respectively. Optimal conditions were determined by using a factor at the time. The maximum reduction in COD was 57 and 70.2% for ozonation (initial pH 9) and UV/O_3 (initial pH of 11), respectively. In H_2O_2/O_3 (initial pH 9, initial concentration of $H_2O_2 = 40$ mM) and UV/O_3/H_2O_2 processes (initial pH of 10, initial concentration of $H_2O_2 = 20$ mM), 65.5 and 82.5% of COD removed, respectively. Reaction time for COD removal of OT solution in all processes was 120 min. Optimal dosage of ozone was 0.5 l/min for all processes based on ozone. Also, after 40 min of reaction, the degradation percent of OT was 100, 90.7, 89.5, and 85.5% for UV/O_3/H_2O_2, UV/O_3, O_3/H_2O_2, and O_3 processes, respectively. The optimum concentration of the OT was obtained at 100 mg/l in all processes. From the kinetic study, it was clear that the mineralization was slower than the degradation and the best process was the UV/O_3/H_2O_2, since it achieved the highest degradation and mineralization efficiency.

Keywords: Advanced oxidation processes (AOPs); Ortho-Toluidine (OT); Degradation; COD (chemical oxygen demand); High-performance liquid chromatography (HPLC)

1. Introduction

O-Toluidine is possibly considered carcinogenic to humans, according to the international agency for research on cancer [1]. Ortho-Toluidine (OT) has been in production over 100 years [2] and also it caused urinary bladder or renal pelvis cancer [3]. O-Toluidine can also be metabolized in a living organism into a number of compounds, some of which are active endotoxins [2].

Due to its various environmental concerns and adverse effects on human health, O-Toluidine has received increasing attention in recent decades [4]. Most of the research available has focused on the toxicity of the OT and its co-mutagenic action with nor Harman [5], rather than the degradation intermediates produced.

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Advanced oxidation processes (AOPs) are based on physicochemical processes that produce powerful oxidative species like hydroxyl radical ($OH^{\bullet}$), whose standard redox potential is 2.8 V. For example, one of the uses of ozone that has grown considerably in recent years is the treatment of water since its action mechanisms do not produce chlorinated compounds that may originate in the chlorine disinfection process. In addition, ozone has a high reduction potential (2.07 V), so it can react with organic compounds slowly and directly. It has been reported that compounds having $-OH$ or $-CH_3$ groups as Ortho or Para substitutes on the benzene ring are activated to electrophilic attack of ozone [6].

In the absence of light, ozone can react directly with an organic substrate, through a slow and selective reaction (Eq. (1)) or through a fast and non-selective radical reaction that produces hydroxyl radicals (Eq. (2)) [6–9]:

$$O_3 + P \rightarrow PO_X \quad (P = \text{pollutant}) \tag{1}$$

$$2O_3 + 2H_2O \rightarrow 2OH^{\bullet} + O_2 + 2HO_2 \tag{2}$$

Some materials such as unsaturated compounds and compounds containing amine groups and acid in acidic solutions react rapidly with ozone. The results support the electrophilic nature of the reaction, either by electrophilic substitution or bipolar Cyclo addition [9]. This route leads to very limited mineralization of the organic compounds, and its use for the removal of pollutants must be reinforced by modification of the method. It has been demonstrated that ozone degraded in aqueous solution by $OH^{\bullet}$, especially when initiated by hydroxide ions (Eqs. (3)–(9)) [10]:

$$O_3 + OH^- \rightarrow O_2 + HO_2^- \tag{3}$$

$$HO_2^- + O_3 \rightarrow O_3^{\bullet -} + HO_2^{\bullet} \tag{4}$$

$$HO_2^{\bullet} \Leftrightarrow O_2^{\bullet -} + H^+ \tag{5}$$

$$O_2^{\bullet -} + O_3 \rightarrow O_3^{\bullet -} + O_2 \tag{6}$$

$$O_3^{\bullet -} + H^+ \rightarrow HO_3^{\bullet} \tag{7}$$

$$HO_3^{\bullet} \rightarrow OH^{\bullet} + O_2 \tag{8}$$

$$O_3 + HO^{\bullet} \Leftrightarrow O_2 + HO_2^{\bullet} \tag{9}$$

The addition of light to the O_3/H_2O_2 process produces a net increase in the efficiency. The two separate processes, UV/O_3 and $UV/H_2O_2/O_3$ were shown to be very effective for the treatment of groundwater and soil remediation [6,7].

Encouraging results using the AOPs (UV/O_3, UV/H_2O_2, and $UV/O_3/H_2O_2$) have been reported [11]. The main problem of the AOPs lies in the high cost of reagents such as ozone, hydrogen peroxide, or energy sources like ultraviolet irradiation. However, the use of solar radiation as an energy source can reduce costs. Moreover, it should be pointed out that when conventional treatment methods are unfeasible, the AOPs normally lead to the best yields in pollutant destruction [12].

The degradation of the OT has been previously investigated by Fenton and electro Fenton processes [13]. In the present study, application of different advanced oxidation processes such as single ozonation, UV/O_3, O_3/H_2O_2, and $UV/O_3/H_2O_2$ was investigated for removal of O-Toluidine in petrochemical wastewater.

2. Materials and methods

2.1. Chemicals and reagents

Ozone was produced in an ozone generator fed with dried oxygen and all reagents were used as received without further purification. O-Toluidine (99.5%), hydrogen peroxide (30%v/v), NaOH, and H_2SO_4 (0.1 M) were reagent grade from Merck. The features of O-Toluidine were shown in Table 1. Distilled water was used throughout this study.

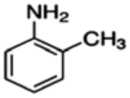
2.2. Apparatus

For UV-based processes, irradiation was performed in a cylindrical photoreactor under a mercury lamp, Philips 15 W (UV-C), which is shown in Fig. 1. The initial pH of the solution was monitored by a pH meter, PT-10P Sartorius Instrument Germany Company. Water bathe, BW20G from Korean company, was used for regulating temperature at 25˚C in all tests and Ozone generator with 214 V and 0.39A from ARDA companies of Iran was employed for the production of ozone.

2.3. Photoreactor

In this project, experiments were carried out in a glass cylindrical semi-batch recirculating photoreactor with one liter of capacity and equipped with a sampling system (Fig. 1). The light source was mercury lamp, which was immersed vertically in the center of the reactor. Ozone was generated by Ozone Generator

Table 1
The molecular properties of O-Toluidine

Pollutant	Molecular formula	Molecular structure	Molecular mass	Solubility in water	Density
O-Toluidine	C_7H_9 N		107.15 (g/mole)	1.5 g/100 mL (25˚C)	1.004 at 20/4˚C (water = 1)

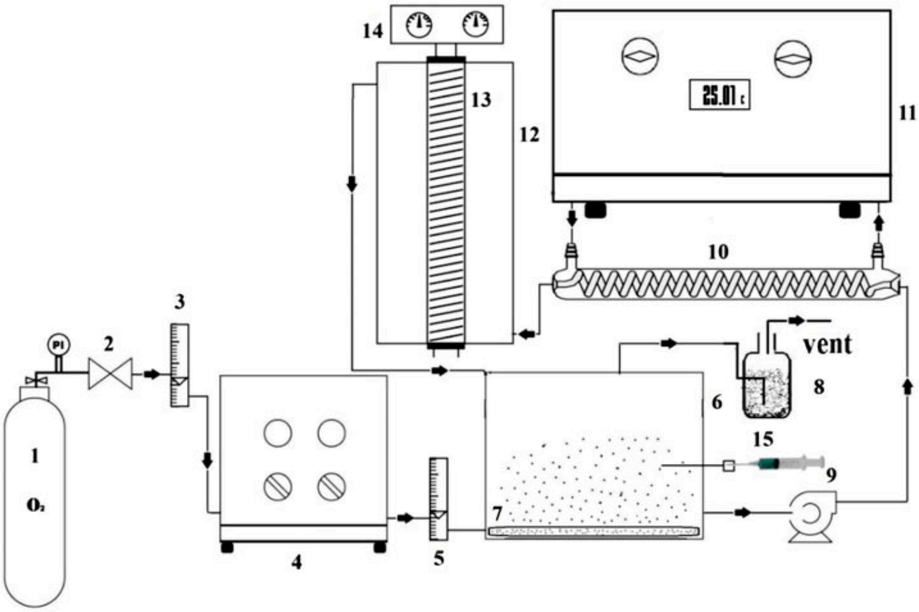


Fig. 1. Experimental setup of the process.
Notes: (1) Pure oxygen capsule, (2) Valve, (3) Rotameter, (4) Ozone generator, (5) Gas flow meter, (6) Reservoir, (7) Ozone sparger, (8) Washing bottle, (9) Circulating pump, (10) Heat exchanger, (11) Thermo bath, (12) Photoreactor, (13) UV-Lamp, (14) Electronic power supply, (15) Sampling system.

with adjustable flow rates and fed by pure oxygen. A flow regulator was used to adjust the oxygen pressure to the inlet of the ozone generator. An ozone generator transferred mixture of oxygen and O_3 from the bottom to the solution in the reservoir by a porous diffuser for well mixing, saturating solution with O_3, better mass transfer and reaction between ozone and pollutant. The reactor was equipped with a water-flow exchanger, using an external circulating flow of a thermostat for regulating temperature at 25˚C in all processes. The solution in the reservoir pumped with the flow rate of 1.5 l/h and entered from beneath to the reactor. After radiation, the solution was recycled back to reservoir from the top of the reactor. The volume of solution in the loop was two liters. The reactor was equipped with a ventilation system to exhaust not reacted ozone. Washing bottle containing 2% (w/w) of KI solution was used.

2.4. Experimental and analytical method

The samples used in the experiments were prepared from a mixture of O-Toluidine and distilled water with its concentration being equivalent to that of the actual onsite wastewater (100 mg/l) and their COD values were checked. COD was measured according to the standard methods [14], a closed reflux with colorimetric methods was developed and spectrophotometer (DR5000, Hach, USA) was used for measuring the absorbance of COD samples in 600 nm.

Exactly 2,000 ml of OT solution was used during each experiment and it was added into the suction of the pump to just fill the reservoir. The discharge stream, after passing through the tube of an exchanger and regulating temperature by thermo bath, was entered from the bottom into the photoreactor. Furthermore, the ozone generator was activated and the ozone was regulated at different flow rates then entered and bubbled through distributor from bottom of the reservoir.

Samples were collected at regular time intervals (20 min) to determine the concentration of O-Toluidine and COD of the effluent. After oxidation reactions, removal of the OT and COD were obtained as (Eqs. (10) and (11)):

$$\text{Removal of OT}\,(\%) = \left(\frac{[\text{OT}]_0 - [\text{OT}]}{[\text{OT}]_0}\right) \times 100 \tag{10}$$

$$\text{Removal of COD}\,(\%) = \left(\frac{[\text{COD}]_0 - [\text{COD}]}{[\text{COD}]_0}\right) \times 100 \tag{11}$$

where $[\text{OT}]_0$ and $[\text{COD}]_0$ were concentration of OT and amount of COD at the start of reaction and [OT] and [COD] were concentration of OT and amount of COD at time t, respectively.

Desired amount of H_2O_2, flow rates of O_3, and dosage of pollutants were prepared. The required amounts of O_3 and H_2O_2 were added into the solution and most experiments were carried out at pH from 4 to 12 in different processes. In ozonation, the reaction time was recorded while starting the injection of ozone to the reactor and for the rest of the experiments adding H_2O_2, starting ozonation and UV lamp occurred spontaneously at the beginning of the reaction. The pH value of the solution was adjusted at desired level by using dilute NaOH and H_2SO_4 (0.1 M).

On the run with H_2O_2, MnO_2 powder was used for eliminating the interference effect of residual H_2O_2 in COD tests and samples were centrifuged to remove MnO_2 powders [15].

2.5. HPLC analysis

The progress in the degradation of the OT was recorded by a high-performance liquid chromatography (Knauer, Germany) equipped with Spectrophotometer (platm blue Germany). A reverse phase column, filled with 3 μm Separon C18, was 150 mm in length and 4.6 mm in diameter. The isocratic method with a solvent mixture of 60% acetonitrile and 40% deionized water with a flow rate of 1 ml/min were used. The wavelength of the UV absorbance detector was 281 nm and the retention time for OT was 4.7 min.

In order to study the degradation of OT in various processes, samples after interval times in optimum conditions were analyzed by HPLC and results were compared with the raw synthesized wastewater. The ratios of peak area for a specific compound in treated and raw samples showed that 93% of OT were degraded and converted to smaller compounds after 30 min of treatment in $UV/O_3/H_2O_2$ process. Finally, the COD values were measured and the efficiencies were calculated with respect to its initial values.

3. Results and discussion

The trends in degradation of OT with different AOPs are presented by showing the effect of pH, the initial dosage of OT, and flow rates of O_3 in ozonation, UV/O_3, O_3/H_2O_2, and $UV/O_3/H_2O_2$ processes.

3.1. The effect of ozone dosage on removal of OT

The use of ozone was characterized as an AOP only when it decomposes to generate hydroxyl radicals (Eq. (2)). Ozone has powerful oxidation ability, so it is able to destroy the structure of organic pollutants and oxidize them to low molecular organics or degrade some organics directly to CO_2 and H_2O_2. It reacts with pollutants in two possible ways, one of them is a direct way that ozone molecules react with dissolved pollutants directly and the other one is the radical way that the reactions between hydroxyl radical generated in the ozone decomposition and the dissolved compounds occurs [16].

In order to evaluate the effect of dosage of ozone on the degradation of OT with O_3, UV/O_3, and $UV/O_3/H_2O_2$, increasing the flow rates of O_3 was applied at pH 9 as shown in Fig. 2.

Dosage of ozone refers to the amount of ozone that flows from the ozone generator into the reservoir and it is an important parameter in treatment of wastewater whereas directly affects the efficiency of degradation and operation cost. Low dosage of ozone results in poor oxidation efficiency and over high dosage leads to the formation of intermediate products which have no or even negative effects on treatment. The oxidation of the OT was due to its reaction with hydroxyl radicals generated in the solution. By increasing flow rates of ozone, the interface between ozone and water was increased and this phenomenon led to enhancement in the concentration of ozone and free radicals in the reservoir; consequently, the degradation rate of OT increased. However, when the ozone concentration in the liquid phase was near to its maximum value (based on the solubility of ozone), amount of ozone flow rate did not affect in the reaction rate and OT removal [17].

The effect of ozone flow rate on the degradation of OT was illustrated in Fig. 2. It is obvious that in low

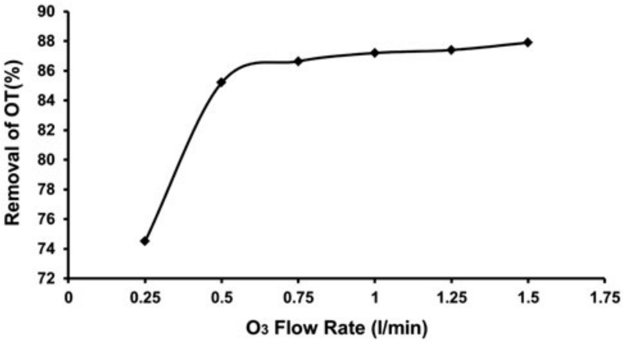


Fig. 2. The effect of ozone dosage on degradation of OT ($[OT]_0$ = 100 mg/l, pH 9, time = 40 min).

ozone flow rates, from 0.25 to 0.5 l/min, degradation increased with sharp slope, but at higher flow rates, ozone exhausted not reacted from the solution and degradation of OT was dependent on flow rates of ozone slightly. Therefore, the optimum flow rate for the mixture of ozone and oxygen was obtained about 0.5 l/min or 2.5 g of pure ozone per hour (according to the document of ozone generator from ARDA Company of Iran and verified by titration with KI solution method). In ozonation process, degradation of the OT were 85.5% after 40 min of reaction at pH of 9 and 100 mg/l of pollutant concentration.

Therefore, many factors affect the process of oxidation with ozone. This paper mainly discusses the effects of dosage of ozone, reaction time, and pH on the oxidation of O-Toluidine.

3.2. Effect of pH on removal of OT

3.2.1. Effect of pH on O_3 and UV/O_3 processes

UV/O_3 process includes aqueous solution saturated with ozone and irradiated by UV light to produce hydrogen peroxide which will also be exposed to UV light and producing hydroxyl radicals (Eqs. (12) and (13)) [18].

$$O_3 + H_2O + hv \rightarrow H_2O_2 + O_2 \tag{12}$$

$$H_2O_2 + hv \rightarrow 2OH^{\cdot} \tag{13}$$

The investigation of experimental results indicated that the oxidation effect of ozone on OT enhanced with rising in pH. However, when pH was higher than 9, the turbidity of samples were increased remarkably, which had an adverse effect on the efficiency of degradation.

The experiments carried out at pH values of 4, 6, 8, 9, 10, 11, and 12 and the results showed that degradation was increased at basic conditions and the optimum pH during this process was 9.

At pH 4, formation of hydroxyl radicals was very low, so radical reactions happened slightly, whereas direct molecular ozonolysis were highly predominant. The double bonds of OT ring seem to be destroyed by ozonolysis and about 85% of OT degraded after 40 min of reaction in optimum pH (Fig. 2). In fact, ozone was reacted with the OT directly at low pH. Whereas, $OH^{\cdot}$ was a strong oxidant originated from the reaction of hydroxide ions with ozone at high pH and it was initiated the chain oxidation reaction of ozone, which was non-selective and very rapid [19]. The ozonolysis products of OT in low pH were oxalic acid and maleic acid and these intermediates were resistant to be mineralized by ozone molecules so removal of COD were low [13].

As pH increased from 4 to 9, both ozonolysis and hydroxyl radical reactions were important. At high pH, the formation of hydroxyl radicals was fast, so ozonolysis was little because of rapid ozone usage for hydroxyl radicals and OH radical was a stronger oxidizing agent than molecular ozone. The overall mineralization efficiency of OT in alkaline pH was more efficient than acidic medium.

In UV/O_3 and O_3 process, about 70.2 and 57% of COD were removed, respectively, after 120 min of reaction. At higher pH, the rate of mineralization drops because O_3 is unstable in high alkaline pH. The removal of COD in O_3 and UV/O_3 process at different levels of pH were presented in Fig. 3.

3.2.2. Effect of pH on removal of OT in O_3/H_2O_2 process

The efficiency of ozone in degradation of O-Toluidine was improved when combined with H_2O_2 or UV radiation.

The addition of hydrogen peroxide to ozonation system provides better results because H_2O_2 accelerates decomposition of ozone (Eq. (14)) by electron transfer through a mechanism shown in a simplified form in the following equations. The process called perozone, combines the direct and indirect ozone oxidation of organic pollutants, the reaction can be considered the activation of H_2O_2 by ozone. It has been suggested that the acceleration of ozonation is due to the fact that H_2O_2 enhances ozone transfer within the water [20–22].

$$O_3 + H_2O_2 \rightarrow OH^{\cdot} + O_2 + HO_2^{\cdot} \tag{14}$$

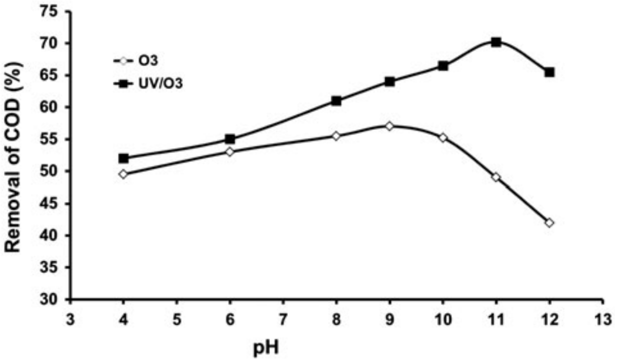


Fig. 3. Changes in COD conversion as a function of pH during O_3 and O_3/UV processes ($[OT]_0 = 100$ mg/l, dosage of ozone = 0.5 l/min, time = 120 min).

$$HO_2^{\bullet} \rightarrow O_2^{\bullet -} + H^+ \qquad (15)$$

$$O_2^{\bullet -} + O_3 \rightarrow O_3^{\bullet -} + O_2 \qquad (16)$$

The pH was a main factor for degradation efficiency and adjusted after adding H_2O_2 to the solution because hydrogen peroxide dissociated in water slightly and produce H^+ therefore cause a little decrease in pH.

In degradation reaction of O-Toluidine, pH was dropped as reaction progressed. The pH varied from 4 to 12. The effect of initial pH on the removal efficiency of O-Toluidine is shown in Fig. 4. For O_3/H_2O_2, it was clear that about 84% of OT degraded in optimum pH (pH 10) and optimum concentration of H_2O_2 (30 mM).

3.2.3. Effect of pH on removal of OT in UV/O_3/H_2O_2 process

This process is a very powerful method which enables complete and fast mineralization of pollutants. It is considered to be the most effective treatment for high-polluted wastewaters [23].

To evaluate the efficiency of each condition on degradation of OT, experiments were carried out under the following conditions:

Also UV light initiates decomposition of H_2O_2 to generate very reactive hydroxyl radicals. pH is a main factor for the degradation efficiency in UV/O_3/H_2O_2 process. In the degradation reaction of O-Toluidine by mentioned process, pH was decreased as reaction advanced [24]. In Fig. 4, the effect of pH in different AOPs was illustrated. For UV/O_3/H_2O_2, 97% of OT degraded in optimum pH (pH 10) and optimum concentration of hydrogen peroxide (30 mM).

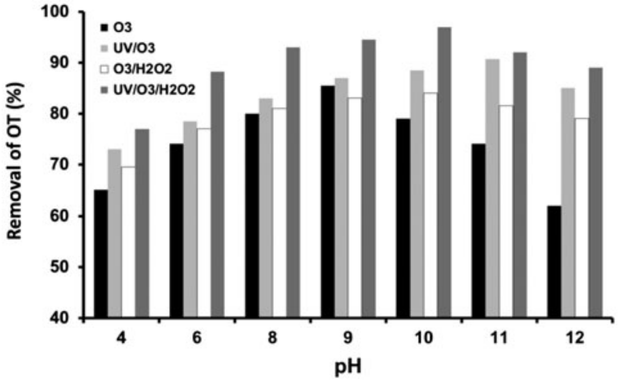


Fig. 4. Effect of pH on degradation of OT in different advanced oxidation processes ($[OT]_0 = 100$ mg/l, dosage of ozone = 0.5 l/min, $[H_2O_2]_0 = 30$ mM, time = 40 min).

3.3. Effect of H_2O_2 concentration on oxidation process

3.3.1. Effect of H_2O_2 dosage on removal of OT in O_3/H_2O_2 process

From Fig. 5, it is clear that increasing concentration of hydrogen peroxide leads to increase in degradation of the OT, the reason can be attributed to enhance in concentration of hydroxyl radicals. The efficiency of the degradation of OT was raised up to a plateau region with increase in initial dosage of H_2O_2; in this condition, additional amount of hydrogen peroxide had no further effect because recombination of hydroxyl radicals happened with excess amounts of H_2O_2. According to the mentioned results, the optimum concentration of hydrogen peroxide obtained was 40 mM in O_3/H_2O_2 process.

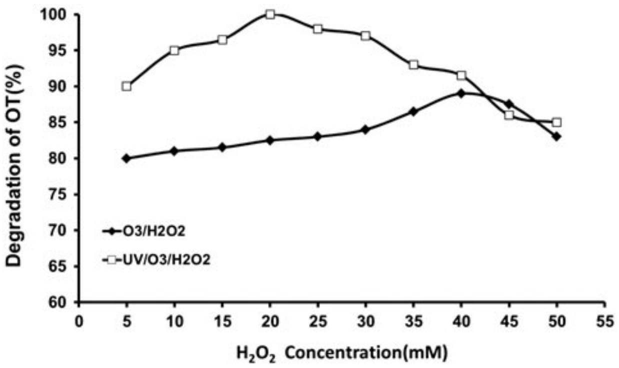


Fig. 5. Influence of initial H_2O_2 concentration on removal of OT (O_3 flow rate at 0.5 l/min, $[OT]_0 = 100$ mg/l, pH 9 for O_3/H_2O_2, and pH 10 for UV/O_3/H_2O_2 process, time = 40 min).

3.3.2. Effect of H_2O_2 concentration on removal of OT in UV/O_3/H_2O_2 process

The effect of initial concentration of hydrogen peroxide on removal of OT in different process was showed in Fig. 5. Experiments were performed by varying the dosage of H_2O_2 from 5 to 50 mM. By increasing the concentration of H_2O_2 from 5 to 20 mM, degradation efficiency increased from 90 to nearly 100% for UV/O_3/H_2O_2 in optimum pH, which may be due to the production of additional $OH^{\cdot}$ radicals originated from O_3 enhanced UV/H_2O_2. The addition of hydrogen peroxide from 20 mM did not improve the removal efficiency. This may be originated from autodecomposition of hydrogen peroxide to oxygen and water and the recombination of hydroxyl radicals. Moreover, higher concentrations of hydrogen peroxide act as free-radical scavenger itself, thereby the concentration of hydroxyl radicals was reduced and efficiency removal of OT decreased [25]. Therefore, H_2O_2 should be added at an optimum concentration to achieve the best results. In O_3/H_2O_2 and UV/O_3/H_2O_2 process, the effect of initial H_2O_2 concentration on degradation of the OT and removal of COD were showed in Figs. 5 and 6.

Results from HPLC showed that O-Toluidine was rapidly degraded the first time of reaction, after that the reaction rate was slower. In UV/O_3/H_2O_2 process, degradation was continued to 93.2% and nearly100% after 30 and 40 min of reaction, respectively. Also, COD was decreased with time, but at a lower rate. As shown in Fig. 6, 82.5% of COD were removed after 120 min of reaction in optimum concentration of hydrogen peroxide, pH and flow rates of ozone. It is considered the most effective treatment for high-polluted wastewaters.

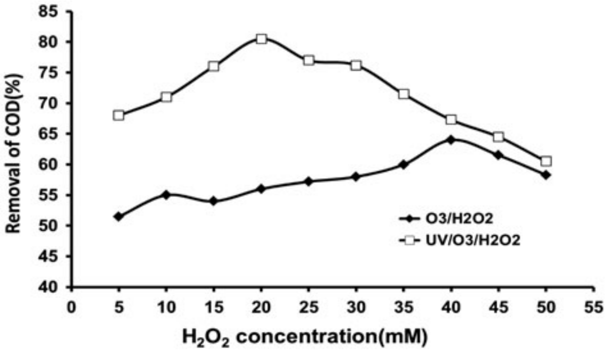


Fig. 6. Influence of initial H_2O_2 concentration on removal of COD (O_3 flow rate at 0.5 l/min, $[OT]_0$ = 100 mg/l, pH 9 for O_3/H_2O_2, and pH 10 for UV/O_3/H_2O_2 process, time = 120 min).

3.4. The effect of initial dosage of OT on degradation efficiency of OT in different AOPs

O-Toluidine (OT) and distilled water were mixed together and solutions with concentration of OT equating to 50, 75, 100, 125, 150, and 175 ml were prepared. The reaction conditions were the same for all cases in which the mixture of ozone and oxygen flow rates were kept at 0.5 l/min.

Degradation of the OT was decreased with an increase in the initial concentration of OT. The proposed reason is that by increasing initial concentration of OT, a large number of OT molecules were reacted with hydroxyl radicals originated from AOP process, and hydroxyl radicals decreased. When the concentration of OT increased, more photons were absorbed by OT molecules and degradation rate decreased.

The effects of initial concentration of OT on degradation efficiency are shown in Fig. 7.

3.5. Comparison of various studied AOPs

A comparison between O_3, O_3/H_2O_2, UV/O_3, and UV/O_3/H_2O_2 process for removal of the OT and COD were illustrated in Figs. 8 and 9.

The effect of pH on degradation of OT by different AOPs is presented in Fig. 4. In case of O_3 and UV/O_3, maximum degradation of OT achieved in alkaline pH at 9.0 and 11, respectively.

The influence of initial dosage of hydrogen peroxide on removal of the OT was shown in Fig. 5. Experiments were executed by changing dosage of H_2O_2 from 5 to 50 mM. In UV/O_3/H_2O_2 process, the maximum degradation was obtained about 93% in an

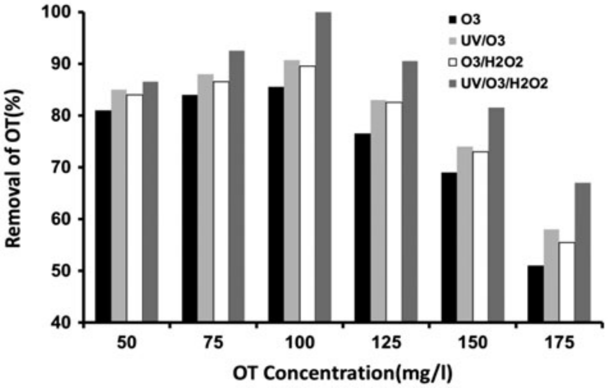


Fig. 7. Effect of different initial concentrations of OT on degradation efficiency (Dosage of ozone at 0.5 l/min, optimum pH for each process, $[H_2O_2]_0$ = 40 and 20 mM for O_3/H_2O_2 and UV/O_3/H_2O_2 process, respectively, time = 40 min).

optimum dosage of H_2O_2 at 20 mM after 30 min of reaction. Excess amounts of H_2O_2 from 20 mM did not improve the degradation efficiency. The reason may be an autodecomposition of H_2O_2 to oxygen and water and recombination of OH radicals. In addition, higher concentrations of H_2O_2 act as a free radical scavenger itself, so decreasing the dosage of hydroxyl radicals and diminishing degradation efficiency [26].

Degradation of OT in four different processes was shown in Fig. 8. After 40 min of reaction, the removal rates for OT were 85.5, 90.7, 89.5, and 100% in the O_3, UV/O_3, O_3/H_2O_2, and $UV/O_3/H_2O_2$, respectively. In all processes, removal efficiency of COD followed the same behavior as O-Toluidine degradation efficiency and amounts of removal of the OT were 57, 70.2, 65.5, and 82.5% in ozonation, UV/O_3, O_3/H_2O_2, and $UV/O_3/H_2O_2$, respectively, after 120 min of reaction. These indicate that $UV/O_3/H_2O_2$ was the best choice and there was a synergetic effect in this system.

3.6. Degradation and mineralization rates of OT

From experimental results, it was obvious that the numbers of hydroxyl radicals were higher than OT. Therefore, hydroxyl radicals can be assumed to be approximately fixed and kinetic constant of reaction was gained by fitting the experimental data using pseudo-first-order kinetic equation. However, when the experimental data were plotted, it looked like a first-order reaction with respect to O-Toluidine decomposition. Therefore, an approach to this kinetic study was done by assuming that the degradation reaction followed first-order kinetics. This approach was in coincidence with similar studies by several authors [27,28]. In this report, reaction kinetics for degradation of chlorophenols pollutant were investigated by different AOPs such as UV/O_3 and UV/ H_2O_2. Exprimental results showed that reactions kinetics were pseudo-first order. In this work, the half-life and constant rate of reaction were obtained and were different from their report because O-Toluidine and chlorophenols had different degradability by AOPs.

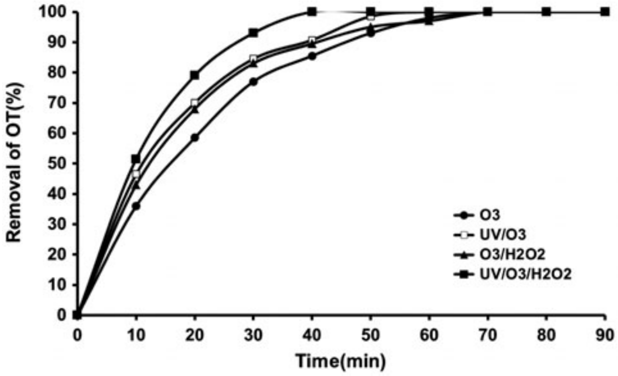


Fig. 8. The Efficiency of degradation of OT in optimum conditions for different processes.

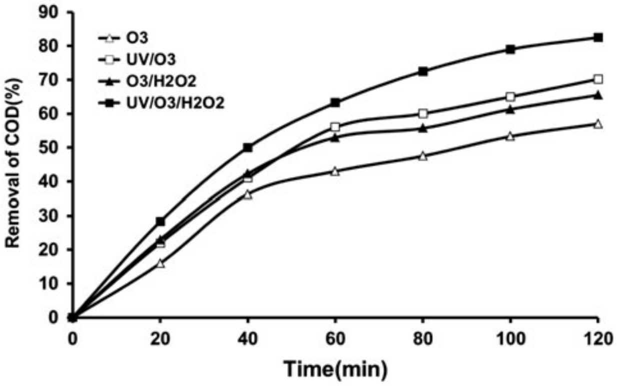


Fig. 9. Effect of different AOPs on mineralization efficiency in optimum conditions.

For evaluating these rate constants, the terms ln $[OT]_0/[OT]$ vs. reaction time were plotted, and after linear regression analysis, the first-order rate constants and half-life of reaction determined were as showed in Table 2.

$$\ln\left(\frac{[OT]_0}{[OT]}\right) = k_{app} \times t \qquad (17)$$

where $[OT]_0$ and $[OT]_t$ are the concentration of the OT at times 0 and t and k_{app} is a pseudo-first-order rate constant and t is the time in minutes. The results approved the significant accelerating effect of $UV/O_3/H_2O_2$ and UV/O_3 reactions on the OT degradation in comparison with other AOPs studied. Almost approximately, all processes followed the pseudo-first-order kinetics and degradation rate of the OT followed the order: $UV/O_3/H_2O_2 > UV/O_3 > O_3/H_2O_2 > O_3$ (Fig. 10).

The raw samples contained 100 mg/l of OT that exerts 280 mg/l of COD. During treatment, COD was

Table 2
Rate constant and half-life of different processes for the removal of OT in optimum conditions

S. No.	Process	$k \times 10^{-3}$ (min^{-1})	$t_{1/2}$ (min)	R^2
1	O_3	49.9	13.9	0.993
2	UV/O_3	59.9	11.57	0.999
3	O_3/H_2O_2	57.7	12	0.999
4	$UV/O_3/H_2O_2$	88.3	7.85	0.997

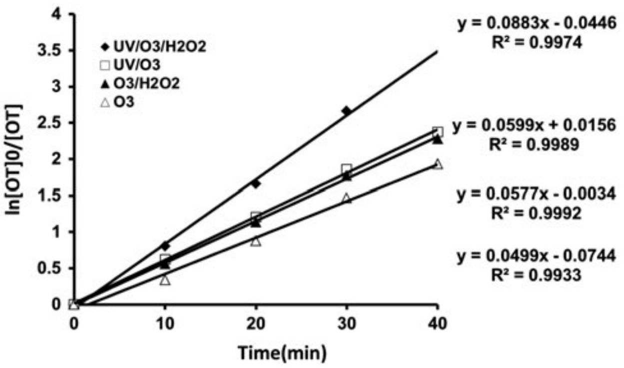


Fig. 10. Degradation of O-Toluidine vs. time for different processes in optimum conditions.

Table 3
Rate constant and half-life time for removal kinetic of COD in optimum condition for different processes

S. No.	Process	$k \times 10^{-3}$ (min^{-1})	$t_{1/2}$ (min)	R^2
1	O_3	7	99	0.954
2	UV/O_3	10.1	68.26	0.971
3	O_3/H_2O_2	8.6	80.6	0.948
4	$UV/O_3/H_2O_2$	14.8	46.8	0.993

decreased in each process, but with a slower rate (Table 3). In different processes, the rate of removal of COD vs. time was investigated too, the term ln $[COD]_0/[COD]$ vs. time were plotted and after linear regression, the half-life time of mineralization reaction and pseudo-first-order rate constant were determined (Fig. 11).

$$\ln\left(\frac{[\text{COD}]_0}{[\text{COD}]}\right) = k_{\text{app}} \times t \tag{18}$$

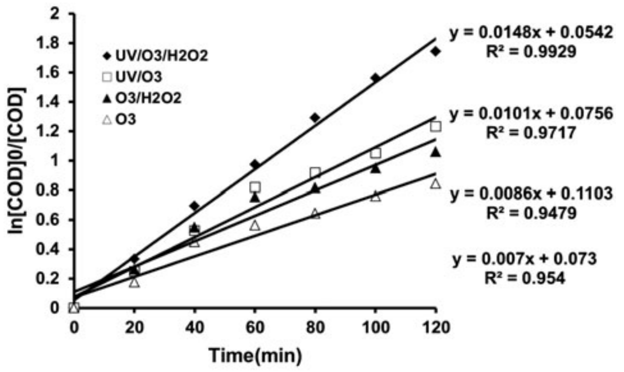


Fig. 11. Removal of COD vs. time for different processes in optimum conditions.

4. Conclusions

Different branches of AOPs such as single oxidants (UV photolysis, O_3, and H_2O_2) and combined processes (UV/O_3, O_3/H_2O_2, and $UV/O_3/H_2O_2$) were studied and compared with each other in the degradation of O-Toluidine in petrochemical wastewater. In addition, different variables (pH, concentration of oxidant and reagent) were investigated to select the best conditions for each process.

Neither UV nor H_2O_2 alone could degrade OT, but by combining UV irradiation with O_3 and H_2O_2, the removal efficiency of COD was increased considerably and followed the same trend as removal efficiency of O-Toluidine but in a lower rate.

pH and concentration of H_2O_2 were two of the main important factors and the optimum pH were obtained about 9, 11, 10, and 10 for O_3, UV/O_3, O_3/H_2O_2, and $UV/H_2O_2/O_3$ and different optimum dosages of H_2O_2 achieved to be 40 and 20 mM for O_3/H_2O_2 and $UV/H_2O_2/O_3$ process, respectively. The result indicated that the protonated form of OT in acidic condition was more resistant to hydroxyl radical than a neutral form of OT in basic condition.

Although ozone and O_3/H_2O_2 process were just more economic than other examined processes, theirs performance were somewhat low so by combining $UV/H_2O_2/O_3$, degradation and mineralization were improved considerably.

Although $UV/O_3/H_2O_2$ was a powerful oxidant for destroying pollutants, but from a kinetic study it was obvious that the rate constant for removal of COD ($k = 0.0148\ \text{min}^{-1}$) was lower than the removal of OT ($k = 0.0883\ \text{min}^{-1}$), because resistant intermediates were formed in treatment process.

Under studied conditions, the relatively high mineralization amount (82.5%) combined with relatively lower costs made $UV/O_3/H_2O_2$ to be the most suitable choice for the degradation of OT from petrochemical wastewaters.

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