RESEARCH ARTICLE

Kinetic Investigation of Degradation of 4-Nitrotoluene in Aqueous Environment by MnO₂/Clinoptilolite/O₃ Process

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Background & Aims of the Study: 4-Nitrotoluene (4NT) is a toxic, resistant, and carcinogenic pollutant. The current study aimed to investigate the degradation and mineralization of 4NT regarded as one of the components of petrochemical wastewater using $MnO_2/Clinoptilolite$ (CP)/O₃ process. The present study also examined the effect of several operational parameters.

Materials and Methods: Synthesized wastewater was used in this study. It is proposed to apply a radical mechanism by the generation of an anion radical $(O_2^{\bullet-})$ prior to hydroxyl radical in order to describe the interaction between ozone and MnO.

Results: The obtained findings of the present study are not similar to those of the ozonation process alone. In ozonation, 4NT removal was positively affected by higher pH due to the formation of hydroxyl radicals. The degradation efficiency values of 4NT in optimum pH for the ozonation and $MnO_2/CP/O_3$ processes were reported as 89.0 and 98.5% within 75 min of reaction, respectively.

Conclusion: In addition, it was obviously shown that the degradation efficiency of 4NT was higher at neutral pH conditions (pH=7) in catalytic ozonation. The removal of the chemical oxygen demand (COD) increased from 50% (only ozonation) to 69.5% (MnO₂/CP/O₃) after 75 min of reaction. The kinetic of degradation was pseudo first-order. Furthermore, the degradation and relative mineralization of 4NT were estimated by high-performance liquid chromatography and COD, respectively.

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Background

Currently, water shortage and quality are great concerns for humans around the world (1). Water shortage affects more than 40% of the worldwide contamination, and this problem will become even more significant with climate alteration (2). 4-Nitrotoluene (4NT) includes one benzene ring attached to nitro and methyl groups. It may actually be carcinogenic in humans or categorized as a significant contaminant based on its toxicity. Therefore, it is essential to develop operative and efficient methods to remove damaging aromatic pollutants from the environment and waste.

Ozonation can be used as a public method for the sterilization and elimination of tastes and odors from water. Furthermore, ozonation is used for the oxidation of organic pollutants to obtain minor biodegradable molecules.

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However, the efficiency of ozone is highly chemistry of reliant on the organic contaminants and amount of O₃ and produced hydroxyl radicals. Ozone selectively reacts with organic combinations and functional groups that have high electron density, including activated aromatic systems, double bounds, reduced sulfur species, and non-protonated secondary and tertiary amines with secondorder rate constants. Nevertheless, one of the main disadvantages of ozonation is the production of oxidation by-products from matrix compounds and micro-contaminants, such as N-nitrosodimethylamine and bromate, which can be sometimes toxic (3).

Ozonation has great significance in water treatment due to its disinfection ability and high oxidation potential of ozone; nonetheless, heterogeneous catalytic ozonation is preferred to single ozonation based on economic and higher removal proficiencies. Therefore, in recent years, there have been studies carried out on heterogeneous catalytic ozonation systems for increasing the efficiency of ozonation. The degradation of many organic mixtures has been investigated using different heterogeneous catalytic methods, including ozonation with activated carbons, zeolites/O₃ (4), TiO₂/O₃ (5), and Al₂O₃/O₃.

Still, there are many polemics concerning investigating the mechanisms of these methods (6-7). For instance, according to some studies, adsorption was proposed as an essential stage in the catalytic ozonation method (8); however, based on other studies, it was suggested that adsorption may negatively affect the catalytic ozonation process. In addition, the impact of the catalyst is uncertain.

Based on the results of previous studies, aqueous ozone can be degraded by catalysts in order to produce hydroxyl radicals (9); however, other studies recommended that catalysts act as adsorbents for both contaminants and ozone to enable surface reactions (10-11). Consequently, it is crucial to identify the catalytic ozonation • Kinetic Investigation of Degradation of 4-Nitrotoluene ...

process to develop this process from laboratory to bench, demo, and industrial scale. Based on the literature, there have been a limited number of studies conducted on the role of MnO₂ in ozonation reactions, especially about the ozone decomposition reaction, indicating a severe lack of information in this regard. The present study aimed to investigate the degradation of 4NT as an aromatic pollutant by the MnO₂/ Clinoptilolite (CP)/O₃ process and effect of pH, initial concentration of 4NT, amount of MnO₂, and kinetics of reaction for higher degradation of 4NT.

Materials & Methods

Materials

All 4NT, hydrogen chloride (HCl), sodium hydroxide (NaOH), potassium iodide (KI), and sodium thiosulfate (Na) were reported as reagent grades and provided by Merck (Merck, the United States). An ozone generator (ARDA Company, Iran) produced ozone by feeding through dry oxygen. Moreover, all the reagents were utilized as received without further purification, and distilled water was applied all over the current study.

Apparatus

A semi-batch (batch for MnO₂ and 4NT and continuous for ozone) reactor was used in order to carry out the experiments. The pure oxygen, from a pressurized capsule, was entered into an ozone generator (214V and 0.39A; ARDA Company, Iran). A 2-liter capacity reactor was equipped with a water-flow jacket connected to a thermostat (BW20G model; Korea) for the adjustment of temperature to 25°C in all the procedures (Figure 1). The pH was calculated by pH Meter PT-10P Sartorius Instrument A Company in Germany. The progress in the degradation of 4NT was recorded by highperformance liquid chromatography (HPLC; Knauer, Germany) equipped with a spectro-

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photometer (Platm blue, Germany).

A reverse-phase column was filled with 3 μ m Separon C₁₈ with a length of 150 mm and diameter of 4.6 mm. The isocratic technique was adopted with adjusted pH to 2.5 by means of orthophosphoric acid and a solvent mixture of acetonitrile and deionized water (60:40% v/v) at a flow rate of 1 ml/min at room temperature. The suspension was centrifuged and filtered for the collection of the catalyst particles in all the experiments.

Catalytic ozonation experiments

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In each run, about 2 L of the aqueous solution, including 75 mg/l of 4NT and nano-MnO₂, were thoroughly mixed in the reactor. A combination of O_3/O_2 was formed by an ozone generator and entered from the bottom of the reactor by a porous diffuser in order to mix well, saturate the solution with O₃, better transfer mass, and react between ozone, MnO₂, and pollutant. The concentration of gaseous ozone was estimated by the iodometric method through the application of 2% neutral buffered potassium iodide for ozone trapping and sodium thiosulfate as a titrant (12). The flow rate of the O₃/O₂ mixture remained constant at

0.3 L min⁻¹ according to the literature and initial experiments, with an ozone concentration of 12.45 mg/L⁻¹. In order to calculate the amount of consumed ozone, the reactor outlet gas was bubbled through a KI (2%w) tamponed solution for the determination of not reacted ozone with the reaction of the potassium iodide solution with the excess ozone according to the following equation:

 $O_3 + 2KI + H_2O \rightarrow I_2 + 2KOH + O_2 \qquad (Equation 1)$

Standard sodium thiosulphate titrated the produced iodine in the presence of starch regarded as an indicator. The amounts of not reacted and reacted ozone were determined, and the value of ozone in tail gas was equivalently obtained. The residual of ozone in an aqueous solution was calculated by a spectrophotometer through the adoption of the indigo method (13).

The MnO₂ particles were dispersed and suspended in the solution as the ozone gas entered the reactor. At different intervals, the withdrawal and filtration of the samples were conducted for the removal of MnO₂ particles. The 4NT concentration was specified using a spectrophotometer at 230 and 280 nm regarded



Figure 1) Schematic diagram of laboratory-scale installation; 1) pure oxygen; 2) cut-off valve; 3) gas flow meter;
4) ozone generator; 5) washing bottle; 6) reactor; 7) magnetic stirrer; 8) ozone diffuser; 9) magnetic bar; 10) sampling port; 11) cooling water supply from thermostat; 12) cooling water return to thermostat

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as two peaks. Similar findings were obtained through HPLC and spectrophotometry methods, particularly at 280 nm, with minor differences between them which were corrected. However, in the acidic pH (i.e., lower than 4), the results of spectrophotometry cannot be associated with HPLC due to ruining the ultraviolet peaks of 4NT in very acidic pH. Only HPLC should be adopted in this state. A pH range of 4-10 was used in order to perform the experiments. The adjustment of the pH was conducted only at the initiation of the reaction by adding NaOH (0.1 M) or HCl (0.1 M). There was a small decrease in pH on the basis of the production of mineral acids.

The chemical oxygen demand (COD) was calculated by means of the standard closed reflux and colorimetric analysis (14). In addition, the absorbance of samples for the COD was estimated by a spectrophotometer (PerkinElmer, USA) at 600 nm. The removal percentage of 4NT as a function of reaction time is obtained using the following equation:

Removal of
$$4NT(\%) = \left(\frac{[4NT]_0 - [4NT]_t}{[4NT]_0}\right) \times 100$$
 (Equation 2)

where $[4NT]_0$ is the initial concentrations of 4NT at the initiation of the reaction, and [4NT] is the concentration of 4NT at time t, respectively.

Results

Effect of pH on MnO₂/O₃ process

Two direct effects of the pH in the $MnO_2/CP/O_3$ system were reported on the process. The first effect is ozone decomposition, and the second impact is surface charge and features of MnO_2 nanocatalyst with a direct influence on their adsorption of pollutant molecules (15, 16). Figure 2 illustrates the effect of pH on the $MnO_2/CP/O_3$ process. According to the experimental results, it was obviously shown that the best findings were achieved at a neutral

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pH during the treatment. The degradation efficiency of 4NT was 98.5% in neutral condition (pH=7) following 75 min of reaction; however, the degradation efficiency values of 4NT were reported as 57.5%, 73.5%, 91%, and 85.3% in the solutions with pH of 4, 6, 8, and 9, respectively. The major factors effective in the degradation of 4NT were reported as surface characteristics and electrostatic interactions between MnO_2 and hydroxide ions in the solution.

Degradation of 4NT by MnO₂/CP/O₃ and O₃ processes

In a study carried out by Ernst et al. (17), it was suggested that the dissolved ozone is firstly adsorbed on the catalyst surface during the catalytic ozonation with Al₂O₃ and then quickly degraded. The $O_2^{\bullet-}$ was produced based on the presence of hydroxyl surface groups resulting in the production of hydroxyl radicals from a series of reactions. In addition, in another study conducted by Zhang et al. (18), it was suggested that $O_2^{\bullet-}$ and hydroxyl radicals were generated by ozone molecule with the hydroxyl group of catalyst.

In the current study, the dissolved molecular ozone was firstly adsorbed on the MnO₂ surface and subsequently decayed into $O_2^{\bullet-}$ and OH^{\bullet} quickly because there were hydroxyl surface groups on the catalyst





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(equations 6 and 7). Furthermore, molecular ozone could be promoted by the produced $O_2^{\bullet-}$ for decomposition into hydroxyl radicals. Afterward, the adsorbed 4NT on the surface of the MnO₂ would be degraded by OH^{\bullet} and molecular ozone (equations 4 and 5). As there is the possibility of ozonation occurrence with MnO₂ through either direct reaction with molecular ozone or indirect reaction with the produced hydroxyl radicals, the removal of the 4NT can be symbolized through the following simple reactions (19):

$O_3 + OT \rightarrow Intermediate \ Product$	(Equation 3)
$OH^{\bullet} + OT \rightarrow Intermediate \ Product$	(Equation 4)
$O_3 + OH^- \rightarrow HO_2^{\bullet} + O_2^{\bullet-}$	(Equation 5)
$0_3 + HO_2^{\bullet} \rightarrow OH^{\bullet} + 2O_2$	(Equation 6)
$O_3 + OH^{\bullet} \rightarrow HO_2^{\bullet} + O_2$	(Equation 7)
$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2$	(Equation 8)

It has been proposed that there is a possibility for ozone to be adsorbed on a catalyst surface in order to yield carious oxidizing species (20). According to the suggested mechanism, it was stated that ozone and organic molecules are adsorbed on the catalyst surface concurrently and ozone degrades on the metallic sites and produces the surface bond radical $(O_2^{\bullet-})$, which is more reactive than ozone resulting in the production of hydroxyl radicals. The oxidation process gradually continues using some oxidized intermediates; however, $O_2^{\bullet-}$ radicals are constantly produced through dissolving ozone transferred to the catalyst surface. There is a reduction in the attraction of the oxidation products to the surface of the catalyst, and final degradation products repulse from the catalyst surface (21).

As it can be observed in Figure 3, the experiments were carried out in 0.9875 for the



Figure 3) Degradation of 4-Nitrotoluene (4NT) in ozonation and catalytic ozonation ([4NT]₀=75 mg L⁻¹; [O₃]₀=12.45 mg L⁻¹; optimum pH for each process; [MnO₂]=1.0 g L⁻¹)

comparative investigation of different processes at optimum pH. Only 5% of 4NT vanished in contact with MnO₂ alone at a pH of 7, resulting from the pollutant adsorption on the surface of nanocatalyst at a catalyst concentration of 1.0 g L^{-1} . Consequently, the 4NT removal rate of the ozone with MnO₂ was reported as higher than the sum of the separate effects of single adsorption and ozonation.

In runs with $MnO_2/CP/O_3$ and O_3 processes, 98.5 and 92.0% of 4NT was removed, respectively. The obtained results demonstrated that the presence of MnO_2 can increase the degradation of 4NT rather than the ozone oxidation alone. Furthermore, the MnO_2 can improve the decomposition of ozone and enhance the formation of hydroxyl radicals. Based on preliminary experiments, approximately 1.0 g L⁻¹ of MnO_2 was utilized because it can initiate the degradation of 4NT, and the aggregation of MnO_2 particles occurred at a high dose of catalysts.

Discussion

Kinetic study

The investigation of other studies has shown that the production of hydroxyl radicals

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originated from ozone decay on the surface of the catalyst resulted in catalytic ozonation (22, 23). However, in case the Mn-Ce-O catalyst was used to increase the removal efficiency of phenolic acids, a different conclusion was obtained according to the results of a study carried out by Quinta-Ferreira and Martins (24). In the aforementioned study, the presence of radical scavengers did not affect the catalytic ozonation efficacy indicating that the reaction in the aforementioned study was not a radical mechanism.

However, in the current study, the kinetic investigation of the degradation of 4NT in the MnO₂/CP/O₃ process was carried out at a pH of 7. According to previous studies, it can be concluded that the possible mechanism for catalytic ozonation consisted of an indirect oxidation reaction with hydroxyl radicals and a direct oxidation reaction after the absorption of 4NT and ozone on the surface of MnO₂. The kinetic relation for the degradation of 4NT using the aforementioned process can be presented as follows:

 $\frac{-d[4NP]}{dt} = ko_3 [4NT][MnO_2][O_3] + k_{OH^{\bullet}}[4NT][MnO_2][OH^{\bullet}]$ (Equation 9)

where $[O_3]$, [4NT], $[OH^{\bullet}]$, and $[MnO_2]$ are ozone concentrations, 4NT, hydroxyl radicals, and MnO₂, respectively. Additionally, ko_3 and $k_{OH^{\bullet}}$ are the rate constants of 4NT with ozone and hydroxyl radicals. At neutral pH, the nonselective reactions of 4NT with hydroxyl radicals were principal; therefore, the kinetic equation can be presented as follows:

$$\frac{-d[4NT]}{dt} = k_{OH} \cdot [4NT] [MnO_2] [OH^{\bullet}]$$
 (Equation 10)

In the above-mentioned process, 4NT was degraded by reaction with MnO_2 and O_3 . Furthermore, the ratio of the concentration of 4NT to O_3 , OH^{\bullet} , or MnO_2 was low; consequently, the concentration of hydroxyl radicals and catalyst can be regarded as

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constant. In the aforementioned states, only the concentration of 4NT changed and the reaction can be supposed to be pseudo first-order (25). Accordingly, the equation can be written as follows:

$$\frac{-d[4NT]}{dt} = k_{OH} \cdot [4NT]$$
 (Equation 11)

where, k'_{OH} is a pseudo first-order rate reaction of 4NT with hydroxyl radicals originated from O₃/nano-MnO₂ procedure. The integration of Equation 11 leads to:

$$-\ln\frac{[4NT]}{[4NT]_0} = \dot{k_{OH}} t \qquad (Equation 12)$$

[4NT] and $[4NT]_0$ where are the concentrations of 4NT in time t and time 0, respectively. As it can be observed in Figure 4, the term $\ln \frac{[4NT]_0}{[4NT]_t}$ and reaction time were plotted, and the obvious first order-rate constants $(k_{OH} = 44.6 \times 10^{-3} min^{-1})$ and half-life of degradation reaction $(t_{1/2} =$ 15.53 min) were determined after linear regression analysis (Equation 12). Through the comparison of the rate constant of the present study with those of previous studies (k = 44.6 $\times 10^{-3} min^{-1}$) (26), it can be concluded that the rate constant is dependent on the type and



MnO₂/Clinoptilolite/O₃ process (pH=7; [MnO₂]=1.0 g L^{-1} ; [O₃]=12.45 mg L^{-1} ; [4-Nitrotoluene]₀=75 mg L^{-1})

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initial concentration of pollutant, dose of ozone, characteristics of the reactor, and catalyst features.

The interaction between MnO₂/CP over ozone is another significant stage in heterogeneous catalytic ozonation. The first supposition is that the existence of the catalyst increases the effective use of ozone and decreases the waste; subsequently, a minor concentration of this oxidant is missing in the off-gas, compared to that reported for the noncatalytic test.

For the investigation of the catalyst capability to decay or adsorb ozone, two runs, including ozone decomposition without catalyst and over MnO₂/CP, were accomplished. In this condition, distillate water was previously saturated with ozone, and the samples were periodically taken to measure dissolved ozone. According to the fact that pH has a high impact on the decomposition of ozone in an aqueous environment (27), the water pH was maintained fixed.

Based on the literature (28-29), Mn and Ce are confirmed to be active for the disintegration of both gaseous and aqueous ozone. Indeed, the presence of MnO₂/CP as a heterogeneous catalyst increased the decomposition of ozone with a high decrease in the concentration of dissolved ozone in the early stages of the catalytic disintegration. For the heterogeneous catalytic disintegration of ozone over metallic oxides, two mechanisms are suggested, including ozone adsorption with further decomposition into hydroxyl radicals or ozone adsorption and decay into surface bonded active oxygen agent as the highly active O^- , which will be accounted for oxidation reactions (30).

Conclusion

The mixture of MnO_2 catalyst and ozone has an important effect on removing 4NT in an aqueous environment. The MnO_2 nanocatalyst quickens the decay of ozone at neutral conditions (pH=7). In the $MnO_2/CP/O_3$ method, the pH is reported to have two direct effects on the process. The first effect is considered the properties of MnO_2 nanocatalyst and surface charge, and the other impact is ozone decay. At neutral pH, the oxidation efficacy of 4NT is greater than that of acidic or alkaline ones. The removal rates of 4NT are reported as 98.5% and 92.0% at 75 min of reaction. In addition, the removal rates of the COD are 69.5% and 50% in $MnO_2/CP/O_3$ and O_3 processes after 75 min of reaction, respectively.

The adsorption and subsequent reaction of 4NT on MnO₂ sites are accountable for the upgrading of the ozonation rate noticed in catalytic runs. The removal rate of 4NT in MnO₂ with ozone was higher than the total of the distinct effects of single ozonation and single adsorption of catalyst (5%) at 1.0 g/l, particularly in the efficiency values of the COD removal (69.5% and 50% in $MnO_2/CP/O_3$ and O_3 process, respectively). According to kinetic investigations, it is clear that in the MnO₂/CP/O₃ process, the rate equation for the degradation of 4NT is pseudo first-order. Moreover, following linear regression, R^2 is gained at 0.9875 and a minor deviation from 1 is originated from supposing the notion that at neutral conditions the selective and direct reactions of ozone are insignificant.

The above-mentioned experimental findings proved the hypothesis that a radical-type mechanism is followed in the removal of 4NT by the O₃/nano-MnO₂ process. According to the proposed mechanism, it was mentioned that organic molecules and adsorbed ozone on the catalyst surface degrade ozone and yield the surface bond radical $(O_2^{\bullet-})$, and they are more reactive than ozone and result in the production of hydroxyl radical which were signified in kinetic equations.

Footnotes

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Conflict of Interest

The authors declare that there is no conflict of interest.

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