

Ultrasound Enhanced Activity of Catalytic Ozonation for Degradation of 2-sec-butyl-4,6-dinitrophenol in Aqueous Solution and Wastewater

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ABSTRACT: *The degradation and mineralization of 2-Sec-butyl-4,6-dinitrophenol (DNBP) in the aqueous solution was investigated by various advanced oxidation processes including US, US/TiO₂, O₃, O₃/TiO₂, O₃/US, and US/O₃/TiO₂. The obtained results revealed that all processes obeyed pseudo-first-order kinetics and the coupled US/O₃/TiO₂ process was the most efficient method for the removal of the pollutant with a high synergistic effect. Then, the effect of major operational parameters, such as the initial DNBP concentration, ozone, and TiO₂ dosage, US power and pH, on the efficiency of the significant coupled process was studied. Total Organic Carbon (TOC) was applied for monitoring the mineralization and lower rate constants were obtained and compared to the degradation rate constants. Finally, four degradation intermediates were identified by the GC-MS method and the mineralization of petrochemical wastewater was monitored by Chemical Oxygen Demand (COD) under optimized conditions.*

KEYWORDS: *Degradation; Mineralization; Ultrasound; Catalytic ozonation; Nano-TiO₂; US/O₃/TiO₂.*

INTRODUCTION

Discharging phenolic compounds, which are classified as persistent organic pollutants (POPs), causes noticeable risks to the human's health and environment. Nitro-substituted phenols like 2-Sec-butyl-4,6-dinitrophenol (DNBP) are toxic and carcinogenic compounds. DNBP is produced in high amounts and used as a herbicide in agriculture and also, as an inhibitor for vinyl aromatics polymerization in petrochemical industry. DNBP can be introduced into the environment during its synthesis and application. Governments restrict

the maximum concentration level (MCL) of DNBP due to its undesirable side effects. The MCL of DNBP in drinking water is 7 ng/mL based on the report provided by the Environmental Protection Agency (EPA) of the USA [1-3]. Therefore, from an environmental point of view, its removal from water sources is essential. DNBP is resistant to biological treatment and other processes like adsorption solely transfer the contaminant to a secondary phase which needs more treatment [4].

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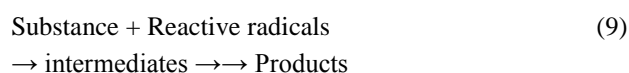
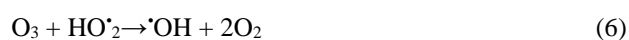
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Application of Advanced Oxidation Processes (AOPs) is more desirable because they can not only oxidize and degrade the various refractory organic contaminants in industrial effluents, but also mineralize them effectively [5]. Free radicals, particularly reactive hydroxyl radicals ($\cdot\text{OH}$), play the main role in oxidizing organic pollutants unselectively to form carbon dioxide (CO_2), water (H_2O) and inorganic mineral salts [6, 7]. Ultrasound (US) method, which is one of the AOPs, has been extensively used for water treatment [8-10]. Ultrasonic waves can produce micro bubbles owing to the cavitation phenomenon in liquids. The resulted bubbles grow and eventually collapse, generating high temperatures and pressures which can decompose water to hydroxyl radicals (Eq. (1)). The advantages of US process, which is a clean method, are safety, high penetration in water medium and significant degradation capability without generating secondary wastes [11-12]. However, it has been found that the degradation rate of contaminants by merely using US is rather slow. Hence, hybrid techniques are used to enhance sonodegradation efficiency [13]. For instance, by adding various catalysts like TiO_2 , which acts as heterogeneous catalyst weak points in the liquid for nucleation, are generated and cavitation bubbles are produced more easily [14]. Therefore, the dissociation reaction of water molecules is enhanced and consequently, the amount of free radicals is increased, resulting in more degradation of the organic compounds. Furthermore, extra hydroxyl radicals are produced by the reaction of electron donors and acceptors with electron-hole pairs generated in semiconductors by the released energy of collapsing bubbles.

The high disinfection and reactivity of ozone (O_3), which is a stronger oxidant compared to oxygen ($E^0=2.07$ V), makes it suitable for usage in water treatment processes [15]. Two possible routes in acidic or basic medium can occur for the degradation of organic contaminants, which are electrophilic reaction of ozone with them or O_3 rapid decomposition to yield $\cdot\text{OH}$ radicals, respectively [16]. However, it has been observed that complete degradation of pollutants may not be achieved by O_3 process [17]. TiO_2 -catalyzed ozonation (O_3/TiO_2) is more effective in comparison with ozone process alone for the degradation of humic and oxalic acid [18]. The enhanced degradation is due to the increase in ozone dissolution and decomposition in the presence of TiO_2 particles [19]. The combination of

ultrasonic irradiation with O_3 is another technique used to degrade a wide variety of biorefractory and persistent contaminants in water more efficiently. The mechanical effects of ultrasound lead to dissolving more ozone from the gas solution to the bulk solution because of the elimination of the mass transfer limitation and then more active radicals can be generated. The following reactions (Eqs. 1-9) have been proposed for the mechanism of US/ O_3 process [20, 21]:



Many researchers have reported the removal of organic contaminants including phenolic compounds such as p-chlorophenol, p-nitrotoluene and m-nitrotoluene in aqueous solutions by the ozone/ultrasound process [22-25]. However, to the best of our knowledge, there is no report on the degradation of DNBP by coupled US/ O_3/TiO_2 process. This process can be considered as a convenient and clean operation for water treatment. The aim of this research was to enhance the degradation and mineralization efficiency of DNBP by the combination of ultrasound with ozone and titanium dioxide. First, the degradation and mineralization kinetics and the efficiency of DNBP removal by various processes including US alone, US/ TiO_2 , O_3 alone, O_3/TiO_2 , O_3/US and US/ O_3/TiO_2 were studied. Then, the effect of the main operational parameters such as the initial DNBP concentration, the initial pH, the power of US, and ozone and catalyst dosages in US/ O_3/TiO_2 process was investigated. Eventually, some degradation intermediates were identified by gas chromatography-mass spectrometry (GC-MS) method and the mineralization of petrochemical wastewater of Tabriz Petrochemical Complex was monitored

during the coupled process under the optimal experimental conditions.

EXPERIMENTAL SECTION

Materials

2-Sec-butyl-4,6-dinitrophenol (DNBP) was purchased from Retell Fine Chemical Co., Ltd. (Tianjin, China) and chosen as an alkyl dinitro phenol compound. Deionized water was used for the preparation of DNBP aqueous solution. Titanium dioxide (Degussa P25, Germany), which had 80% anatase and 20% rutile phases, with the average size of 21 nm and the surface area of $50 \pm 15 \text{ m}^2/\text{g}$ was utilized as the nano-catalyst. All other chemicals were obtained from Merck, Germany.

Experimental set-up and procedure

The experimental set-up was illustrated in Fig. 1. Experiments were performed in a batch cylindrical quartz reactor with the inner diameter of 80 mm and the volume of 500 mL. The pH of the solution was adjusted by adding sodium hydroxide or perchloric acid. The ultrasonic processor (Hielscher, UP 400S, Germany) with variable power control was equipped with a 24-kHz converter and a pure titanium probe (the tip diameter of 14 mm, the height of 100 mm). Calorimetric method was applied to measure the entering ultrasonic power to the solution (Eq. 10):

$$\text{Power} = (dT/dt) C_p M \quad (10)$$

For a sonochemical system, temperature (T) was measured versus time (t) and then from the depicted plot, (dT/dt) could be estimated; moreover, C_p and M were heat capacity (J/kg.K) and the mass of the solvent (kg), respectively. Actual power dissipation in the volume of the solution was determined as 0.09, 0.25 and 0.4 W/mL for the utilized US power of 80, 240 and 400 W, respectively [17]. The glass cylinder was sealed with a polyethylene cap during operation. The probe was fixed at the center of the polyethylene cap and immersed in the solution. Ozone, which was supplied from the ozone generator (Donali, Iran), was fed to the reactor by a diffuser from its bottom. The concentration of ozone was adjusted by varying the power and measured by KI method [26]. The experiments were performed in a temperature controlled bath. In each experiment, 250 mL of a reaction mixture containing a certain concentration of DNBP and TiO_2 (in processes which had TiO_2)

was prepared. Then, the solution was treated by the chosen O_3 dose and/or US power density. The samples were withdrawn by a glass syringe at distinct reaction time-intervals, centrifuged and filtered for the separation of TiO_2 particles (if they were existed). Finally, the sample was analyzed for the degradation of DNBP concentration. The experimental conditions of experiments have been summarized in Table 1.

Analytical methods

The concentration of DNBP (C) was determined by high performance liquid chromatography (HPLC) (Shimadzu, SCL-6A, Japan). A ZOBAX column (5 μm C18) and the mobile phase of methanol/water (7:3 v/v) with the flow rate of 1 mL/min were applied in HPLC analysis. The mineralization of DNBP was monitored by total organic carbon (TOC) using catalytic oxidation method (Shimadzu TOC-5000, Japan). Chemical Oxygen Demand (COD) was analyzed using open reflux method [27] for DNBP aqueous solution and petrochemical wastewater containing DNBP. GC-MS analysis (Agilent Technologies, Palo Alto, Canada) was utilized to identify the degradation intermediates of DNBP by US/ O_3 / TiO_2 process. It should be noted that N,O-bis-(trimethylsilyl)acetamide was applied after the extraction of intermediates to yield silylated products which could be determined more suitably by GC-Mass method. An Agilent 6890 gas chromatography with a 30 m to 0.25 mm HP-5MS capillary column coupled with an Agilent 5973 mass spectrometer operating at 70 eV was applied. The resulting silylated products were analyzed by GC-MS by the temperature program of 50 °C for 4 min, 8 °C/min up to 300 °C and the hold time of 4 min. The temperatures of the inlet, transfer line and detector were 250, 250 and 300 °C, respectively [28].

RESULTS AND DISCUSSION

Comparison of different processes for the degradation of DNBP and kinetics study

The degradation efficiency (DE%) is defined as the percentage ratio of degradation amount ($C_0 - C$) of DNBP at a certain process time (C) to its initial concentration (C_0). The degradation and mineralization of DNBP (40 mg/L) with US, US/ TiO_2 , O_3 , O_3 / TiO_2 , US/ O_3 and US/ O_3 / TiO_2 processes are demonstrated in Fig. 2a and b. The US alone process led to merely 1.3% of DNBP degradation after the process time of 9 min, indicating that the US had a weak effect on the degradation of DNBP.

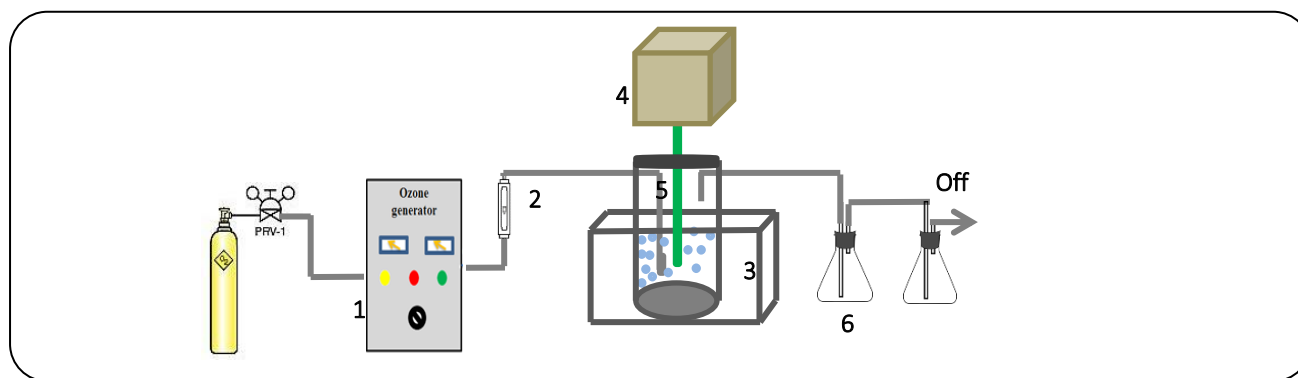


Fig. 1: The experimental set-up: (1) ozone generator; (2) rotameter; (3) temperature controlled bath; (4) ultrasonic generator; (5) reactor (6) absorption bottle.

Table 1: Experimental conditions of experiments.

Parameters	Values
DNBP initial concentration (mg/L)	20-50
US Power density (W/mL)	0.09-0.4
TiO ₂ dosage (mg/L)	30-60
O ₃ concentration (mg/L)	2.3-60

O₃ alone process was more effective than the US alone process, in which 70.9% of DNBP was degraded after 9 min. However, the degradation efficiency of the US combined with O₃ exceeded the sum of O₃ and US alone techniques (97.3% at 9 min). Also, the same trend was observed for TOC removal, in which 57.2% of TOC was eliminated by US/O₃ in comparison with US (1.5%) and O₃ (31.6%) after 45 min of the process. During ozonolysis without sonication, ozone moved from the gas phase into the solution and then reacted in the bulk solution either directly with the substrate or indirectly *via* reactions with radicals generated by O₃ auto decomposition, like hydroxyl radicals, depending on the pH of the solution [29]. In sonolysis alone, the substrate could undergo direct pyrolysis, and/or secondary reactions took place between the substrate and the reactive radicals produced from the pyrolysis of H₂O in a cavitation bubble. However, in the combined system, additional pathways could occur by the direct interaction of sonolysis and ozonation [30]. Sonolysis could enhance the decomposition of O₃, resulting in the generation of more $\cdot\text{OH}$ radicals to react with the substrate (Eqs. 2 and 3). Moreover, US could enhance the mass transfer of O₃, causing the extra O₃ to be transferred to the solution [31]. Using TiO₂ in combination with US, O₃ and US/O₃

processes showed 4%, 73.1% and 98.99% degradation of DNBP after the reaction time of 9 min, thereby implying the synergistic effect of TiO₂. The presence of TiO₂ could enhance the dissociation reaction of H₂O molecules (Eq.(1)) to increase the generated amounts of free radicals, thereby promoting the degradation rate of the DNBP [32]. The enhanced effect of TiO₂ on US/O₃ process for mineralization was more discernable than its degradation (Fig. 2 a and b).

Under the described experimental conditions, the degradation and mineralization of DNBP obeyed the pseudo-first-order kinetics for all applied AOPs. The reaction can be described by $\ln(C/C_0) = -k_{\text{app}}t$, where k_{app} is the apparent pseudo-first-order reaction rate constant. In all AOPs processes, the straight lines confirmed the proposed kinetics (Table 2). The k_{app} was 0.498 min⁻¹ for the US/O₃/TiO₂ process, considerably higher than the sum of the US ($k=0.001$ min⁻¹) and O₃/TiO₂ ($k=0.137$ min⁻¹) process (Table 2), implying a high synergistic effect between US and O₃/TiO₂. The synergistic effect of the mentioned processes, which was 0.72, was determined using the following equation by the apparent pseudo-first-order rate constants:

$$\text{Synergy} = \left(K_{\text{US/O}_3/\text{TiO}_2} - (k_{\text{US}} + k_{\text{O}_3/\text{TiO}_2}) \right) / K_{\text{US/O}_3/\text{TiO}_2} \quad (11)$$

Furthermore, similar kinetics and efficiency order were observed for the mineralization of DNBP by the above-mentioned AOPs, which were monitored by TOC removal after 45 min of treatment; the k_{app} for the mineralization of DNBP was determined by the same method ($\ln(\text{TOC}/\text{TOC}_0) = -k_{\text{app}}t$), as presented in Table 2 [32]. The synergistic effect of US and O₃/TiO₂ was also noticeable for DNBP mineralization and was calculated

Table 2: Pseudo-first order degradation and mineralization rate constants of DNBP in various processes.

Treatment process	Degradation rate constant (min ⁻¹)	Correlation coefficient (R ²)	Mineralization rate constant (min ⁻¹)	Correlation coefficient (R ²)
US	0.001	0.935	0.0004	0.970
US/TiO ₂	0.004	0.977	0.0009	0.994
O ₃	0.137	0.998	0.008	0.967
O ₃ /TiO ₂	0.149	0.997	0.011	0.909
US/O ₃	0.395	0.921	0.018	0.923
O ₃ /US/TiO ₂	0.498	0.912	0.024	0.944

[DNBP]₀ = 40 mg/L, pH = 6.5, T = 25 °C, O₃ concentration = 5.2 mg/L, US power density = 0.4 W/mL and TiO₂ dosage = 50 mg/L

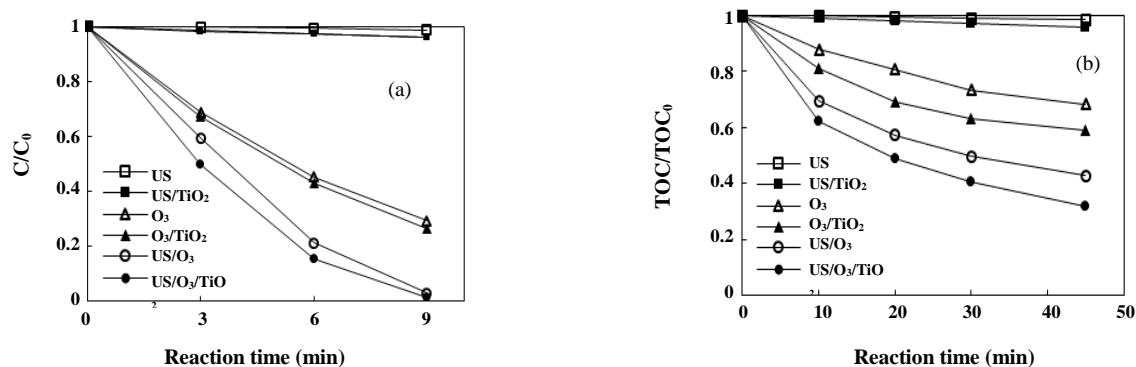


Fig. 2: (a) Degradation curves of DNBP and (b) removal of TOC by various oxidation processes. Experimental conditions: pH = 6.5, 50 mg/L TiO₂, C₀ = 40 mg/L, ozone gas concentration = 5.2 mg/L and US power density = 0.4 W/mL.

to be 0.52 with the mineralization rate constants (Eq. (11)). By comparing data in Table 2, it was found that the mineralization rate was slower than degradation rate in an AOP at the same experimental conditions owing to the produced intermediates during the processes, which were needed to be degraded completely to water, carbon dioxide and inorganic salts [32]. As a consequence, other experiments for DNBP degradation were performed by the combination of US and O₃/TiO₂ processes.

The influence of experimental parameters on US/O₃/TiO₂ process and intermediates identification

The effect of experimental parameters including the initial DNBP concentration, ozone and TiO₂ dosage, US power density and pH on the degradation and mineralization of DNBP was studied. Degradation and mineralization of DNBP were decreased by increasing DNBP concentration (Fig. 3) due to the identical amount of oxidizing species produced at the same conditions to react with more DNBP molecules and its degradation

intermediates [15]. By increasing the O₃ dosage, the degradation and mineralization of DNBP were enhanced since the mass transfer of O₃ was improved and more oxidizing species like hydroxyl radicals were generated (Fig. 4) [16]. The effect of TiO₂ dosage on the DE% and TOC has been plotted in Fig. 5. It can be concluded that both DE% and TOC were not altered noticeably by increasing TiO₂ dosage up to an optimum amount and as a result, the dosage of 50 mg/L was selected as the desired one. This could be attributed to more scattering of ultrasound in the presence of an excessive amount of TiO₂ particles [33].

The influence of US power density on the degradation and mineralization of DNBP is demonstrated in Fig. 6. DNBP had a high boiling point; therefore the interfacial region between microbubbles and bulk solution was the most significant area for the degradation of DNBP by hydroxyl radicals attack. By increasing the power density, more cavitation bubbles and consequently, more reactive radicals were generated. Thus, degradation of

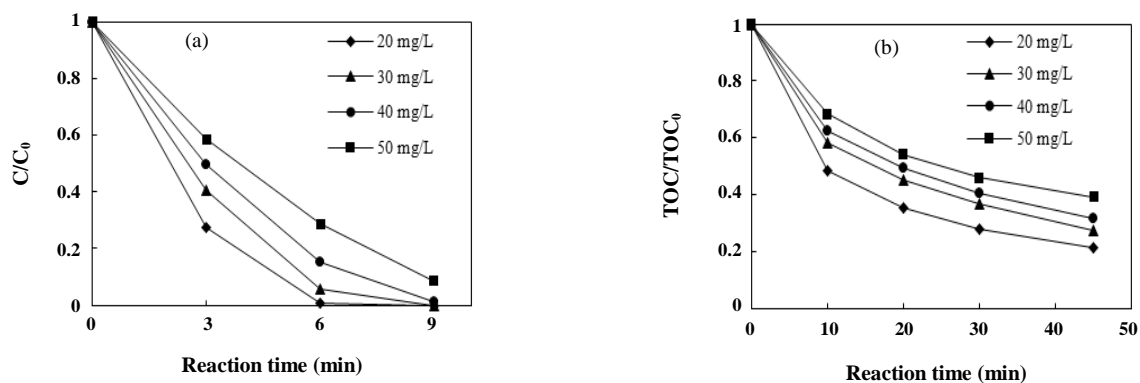


Fig. 3: Effect of initial DNBP concentration on (a) degradation of DNBP, and (b) removal of TOC by the $US/O_3/TiO_2$ process. Experimental conditions: 50 mg/L TiO_2 , pH = 6.5, ozone dosage = 5.2 mg/L and US power density = 0.4 W/mL.

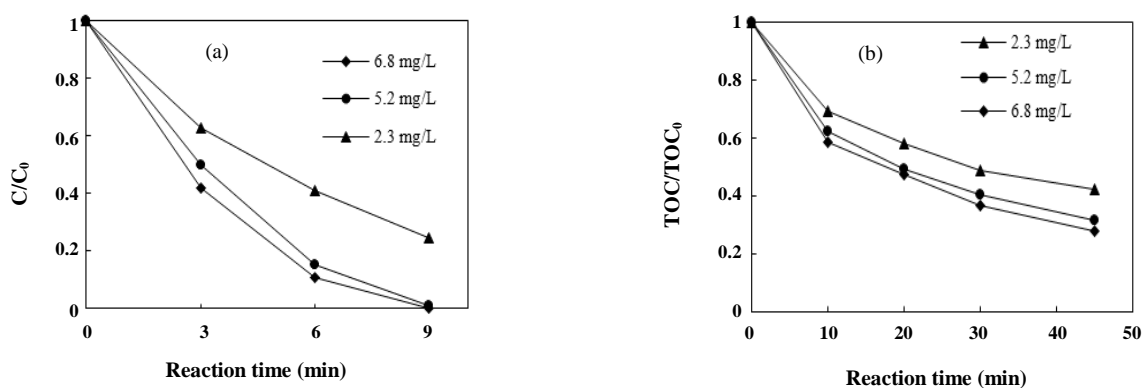


Fig. 4: Effect of ozone dosage on (a) degradation of DNBP, and (b) removal of TOC by the $US/O_3/TiO_2$ process. Experimental conditions: pH = 6.5, 50 mg/L TiO_2 , $C_0 = 40$ mg/L and US power density = 0.4 W/mL.

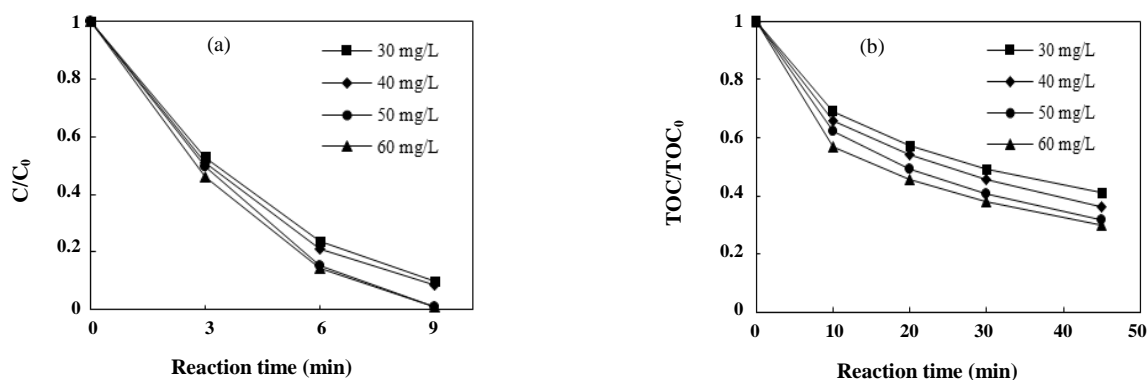


Fig. 5: Effect of catalyst dosage on (a) degradation of DNBP, and (b) removal of TOC by the $US/O_3/TiO_2$ process. Experimental conditions: pH = 6.5, $C_0 = 40$ mg/L, ozone dosage = 5.2 mg/L and US power density = 0.4 W/mL.

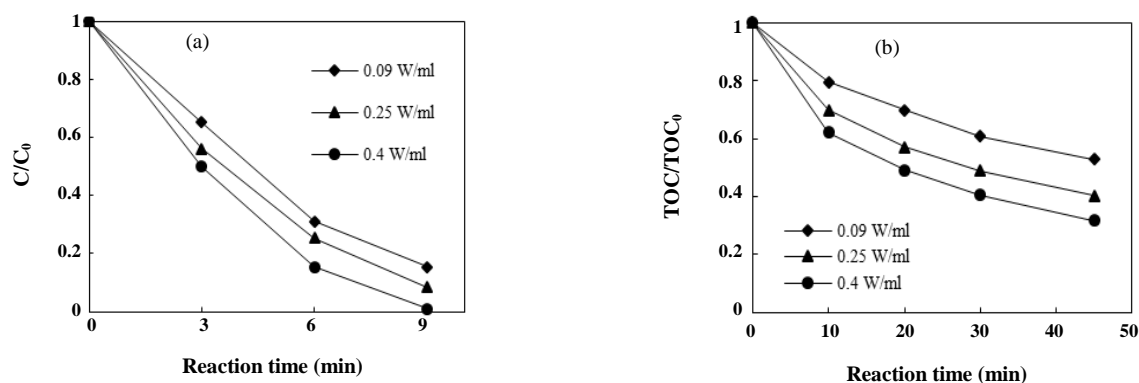


Fig. 6: Effect of US power on (a) degradation of DNBP, and (b) removal of TOC by the US/O₃/TiO₂ process. Experimental conditions: pH = 6.5, 50 mg/L TiO₂, C₀ = 40 mg/L and ozone dosage = 5.2 mg/L.

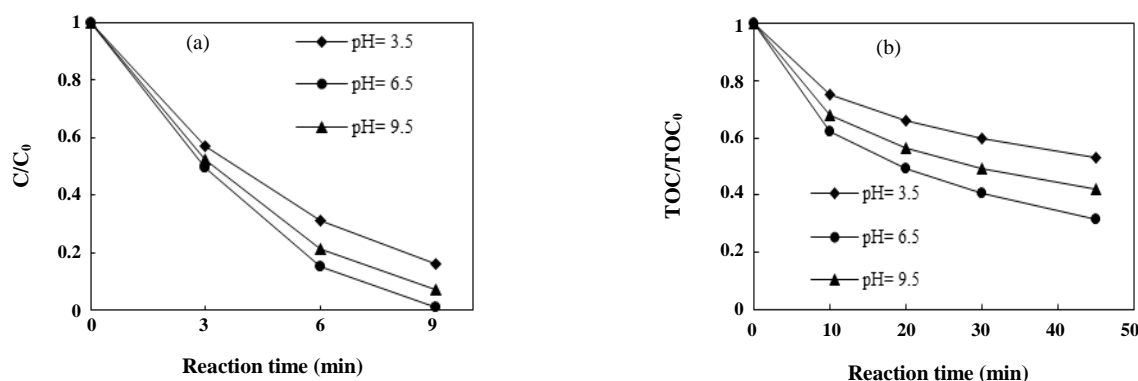


Fig. 7: Effect of initial solution pH on (a) degradation of DNBP, and (b) removal of TOC by the US/O₃/TiO₂ process. Experimental conditions: 50 mg/L TiO₂, C₀ = 40 mg/L, ozone dosage = 5.2 mg/L and US power density = 0.4 W/mL.

DNBP was enhanced. However, by the further increase in the US power density, degradation enhancement was lowered because O₃ degassing occurred in higher rates [34]. The DE% and TOC removal of DNBP was studied in the pH of 3.5, 6.5 and 9.5 (Fig. 7).

The degradation of DNBP approximately showed the same results in the pH of 6.5 and 9.5, but the pH of 6.5 demonstrated the best performance for the mineralization of DNBP. In acidic medium (pH= 3.5), the ozone molecule was the predominant form in the solution, which could degrade organic pollutants by the direct electrophilic attack, which was generally less effective than alkaline medium [35]. The relatively lower TOC removal efficiency at alkaline conditions (pH= 9.5) could be explained by the scavenging effect of generated t-butyl radicals from DNBP degradation on hydroxyl radicals, so the pH of 6.5 was the desired pH value for the

degradation of DNBP. All apparent rate constants for the degradation and mineralization of DNBP under various operational conditions were calculated by the pseudo-first order kinetics assumption, as presented in Table 3. In general, in AOPs, the mineralization rate was less than degradation rate at the identical operational conditions owing to the generated intermediates during the process, which were required to be oxidized and mineralized [32].

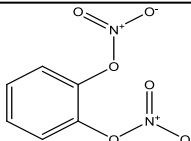
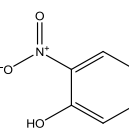
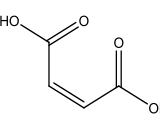
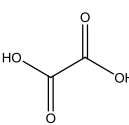
In order to identify the intermediates in US/O₃/TiO₂, 250 mL of DNBP (40 mg/L) was treated for 6 min at the desired conditions. Then the intermediates were extracted and detected by GC-MS method. Four generated intermediates were recognized by the comparison with the commercial standards, as presented in Table 4. However, several intermediates could not be identified because of the quick oxidization to other derivatives or the low match factor of chromatographic peaks [36-37].

Table 3: Effect of the operational parameters on the apparent pseudo-first-order constants of degradation and mineralization for O₃/US/TiO₂ process.

Operational parameters and amounts	Degradation rate constant (min ⁻¹)	Correlation coefficient (R ²)	Mineralization rate constant (min ⁻¹)	Correlation coefficient (R ²)
DNBP concentration (mg/L)				
20	0.817	0.931	0.032	0.907
30	0.77	0.903	0.027	0.942
40	0.498	0.912	0.024	0.944
50	0.269	0.965	0.02	0.932
US density (W/mL)				
0.09	0.211	0.987	0.013	0.969
0.25	0.273	0.98	0.019	0.948
0.4	0.498	0.912	0.024	0.944
TiO ₂ dosage (mg/L)				
30	0.258	0.995	0.019	0.939
40	0.277	0.995	0.021	0.947
50	0.498	0.912	0.024	0.944
60	0.507	0.919	0.025	0.912
O ₃ concentration (mg/L)				
2.3	0.154	0.999	0.018	0.932
5.2	0.498	0.912	0.024	0.944
6.8	0.688	0.873	0.027	0.947

Amount of operational parameters, except the conditions mentioned above: [DNBP]₀ = 40 mg/L, pH = 6.5, T = 25 °C, O₃ concentration = 5.2 mg/L, US power density = 0.4 W/mL and TiO₂ dosage = 50 mg/L

Table 4: Identified intermediates during US/O₃/TiO₂ process.

	Dinitro catechol
	Nitrophenol
	Maleic acid
	Oxalic acid

Reusability of the catalyst and Mineralization of a real wastewater by US/O₃/TiO₂ process

The potential of the catalyst in successive application and the utilization of a treatment process for the mineralization of a real wastewater can be significant from a practical point of view. Hence, three repetitive experiments were carried out for the degradation of DNBP under the obtained desired conditions. After each run, the utilized catalyst was recovered and dried for the next run. As can be seen in Fig. 8, the degradation amount was the same after three repetitions. This confirmed not only the reusability and stability of the catalyst, but also the reliability of the results for the O₃/US/TiO₂ process.

The wastewater with yellow color (20 times diluted and initial COD = 1053 mg/L), which had approximately 40 mg/L of DNBP, was provided by Petrochemical

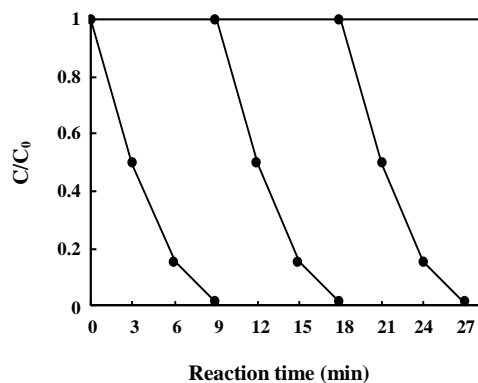


Fig. 8: Reusability profiles during repetitive runs.

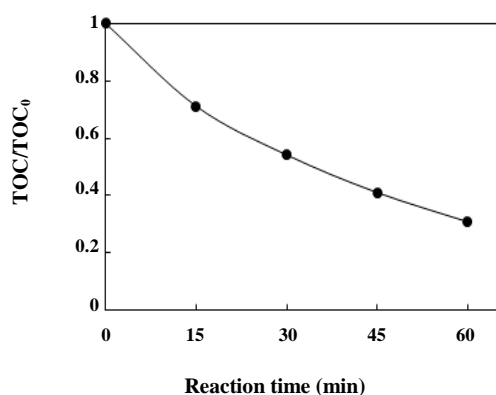


Fig. 9: COD removal for real wastewater by the US/O₃/TiO₂ process.

complex (Tabriz, Iran). COD removal of 69.1% was observed after 60 min of treatment, confirming the destruction of organic pollutants in the wastewater (Fig. 9).

CONCLUSIONS

The novel coupled US/O₃/TiO₂ process was applied for the degradation and mineralization of DNBP and compared with US, US/TiO₂, O₃, O₃/TiO₂, and US/O₃ processes. All processes followed pseudo-first-order kinetics. The results revealed that the US/O₃/TiO₂ was the most effective process for this purpose. The degradation and mineralization of DNBP was enhanced by increasing US power, TiO₂ dosage, and ozone concentration and declined by increasing the DNBP concentration. Moreover, the desired condition was chosen for the treatment of DNBP at the pH of 6.5, the Us power of 0.4 W/mL, TiO₂ dosage of 50 mg/L and ozone concentration of 5.2 mg/L. Total organic carbon elimination

was monitored during the processes to study the mineralization of DNBP and the same data were observed with lower rates, compared to degradation rates, at the same operational conditions owing to the degradation intermediates. Under the optimal condition, the degradation efficiency of 98.99% after 9 min and TOC decay of 68.40% after 45 min were observed for the treatment of DNBP (40 mg/L). Four degradation intermediates were identified by GC-MS, indicating the degradation of the contaminant and the generated intermediates. Finally, this process was utilized for the mineralization of DNBP in petrochemical wastewater (with the initial COD of 1053 mg/L) properly by monitoring chemical oxygen demand removal and COD elimination of 69.1% was obtained after 60 min of treatment.

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REFERENCES

- [1] Nakajima J., Tazikani S., Tomioka H., [Retardation Effect of Sulfonic Acid on Thermal Radical Polymerization of Styrene](#), *Jpn Petrol Inst*, **46**: 359–367 (2003).
- [2] Gasiewicz T.A., “[Nitro Compounds and Related Phenolic Pesticides](#)”, In: Hayes WJ., Laws E.R.J. (Eds.). “[In Handbook of Pesticide Toxicology](#)”, Academic Press, San Diego., **3**: 1191–1269 (1991).
- [3] U.S. Environmental Protection Agency. Lab Cert Bulletin, EPA-815-N-00-001a. (2000).
- [4] Ayranci E., Hoda N., [Adsorption Kinetics and Isotherms of Pesticides onto Activated Carbon-Cloth](#), *Chemosphere*, **60**:1600-1607 (2005).
- [5] Khataee A.R., Zarei M., [Photocatalysis of a Dye Solution Using Immobilized ZnO Nanoparticles Combined with Photoelectrochemical Process](#), *Desalination*, **273**: 453-460 (2011).
- [6] Pera-Titus M., García-Molina V., Baños M.A., Giménez J., Esplugas S., [Degradation of Chlorophenols by Means of Advanced Oxidation Processes: A General Review](#), *Appl. Catal. B Environ*, **4**: 219-256 (2004).

- [7] Gogate P.R., Pandit A.B., [A Review of Imperative Technologies for Wastewater Treatment I: Oxidation Technologies at Ambient Conditions](#), *Adv. Environ. Res.*, **8**:501-551 (2004).
- [8] Hao H., Chen Y., Wu M., Wang H., Yin Y., Lu Z., [Sonochemistry of Degrading p-chlorophenol in Water by High-Frequency Ultrasound](#), *Ultrason. Sonochem.*, **11**:43-46 (2004).
- [9] Madhavan J., Kumar P.S., Anandan S., Grieser F., Ashokkumar M., [Sonophotocatalytic Degradation of Monocrotophos Using TiO₂ and Fe³⁺](#), *J. Hazard. Mater.*, **177**:944-949 (2010).
- [10] Wang J., Guo Y., Liu B., Jin X., Liu L., Xu R., Kong Y., Wang B., [Detection and Analysis of Reactive Oxygen Species \(ROS\) Generated by Nano-Sized TiO₂ Powder under Ultrasonic Irradiation and Application in Sonocatalytic Degradation of Organic Dyes](#), *Ultrason. Sonochem.*, **18**:177-183 (2011).
- [11] Behnajady M.A., Modirshahla N., Shokri M., Vahid B., [Effect of Operational Parameters on Degradation of Malachite Green by Ultrasonic Irradiation](#), *Ultrason. Sonochem.*, **15**:1009-1014 (2008).
- [12] Wang J., Sun W., Zhang Z., Zhang X., Li R., Ma T., Zhang P., Li Y., [Sonocatalytic Degradation of Methyl Parathion in the Presence of Micron-Sized and Nano-Sized Rutile Titanium Dioxide Catalysts and Comparison of Their Sonocatalytic Abilities](#), *J. Mol. Catal. A Chem.*, **272**:84-90 (2007).
- [13] Xiong Z.L., Cheng X., Sun D.Z., [Pretreatment of Heterocyclic Pesticide Wastewater Using 256 Ultrasonic/Ozone Combined Process](#), *J Environ Sci-China*, **23**:725-730 (2011).
- [14] Zatloukalová K., Obalová L., Kočí K., Čapek L., Matěj, Z. Šnajdhaufová, H. Ryzkowski, J.; Słowik, G. [Photocatalytic Degradation of Endocrine Disruptor Compounds in Water over Immobilized TiO₂ Photocatalysts](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **36**(2): 29-38 (2017).
- [15] Mousanejad T., Khosravi M., Tabatabaai S., Khataee A.R., Zare K., [Photocatalytic Ozonation for Degradation of 2-sec-butyl-4, 6-dinitrophenol \(DNBP\) Using Titanium Dioxide: Effect of Operational Parameters and Wastewater Treatment](#), *Res. Chem. Intermed.*, **40**:711-722 (2014).
- [16] Yang T., Peng J., Zheng Y., He X., Hou Y., Wu L., Fu X., [Enhanced Photocatalytic Ozonation Degradation of Organic Pollutants by ZnO Modified TiO₂ Nanocomposites](#), *Appl. Catal. B Environ.*, **221**: 223-234 (2018)
- [17] He Z., Song S., Ying H., Xu L., Chen J., [p-Aminophenol Degradation by Ozonation Combined with Sonolysis: Operating Conditions Influence and Mechanism](#), *Ultrason. Sonochem.*, **14**:568-574 (2007).
- [18] Hu Y., Milne N., Gray S., Morris G., Jin W., Duke M., Zhu B., [Combined TiO₂ Membrane Filtration and Ozonation for Efficient Water Treatment to Enhance the Reuse of Wastewater](#), *Desal. Wat. Treat.*, **34**: 57-62 (2011).
- [19] Pang Y. L., Abdullah A.Z., Bhatia S., [Review on Sonochemical Methods in the Presence of Catalysts and Chemical Additives for Treatment of Organic Pollutants in Wastewater](#), *Desalination*, **277**: 1-14 (2011).
- [20] Vecitis C.D., Lesko T., Colussi A.J., Hoffmann M.R., [Sonolytic Decomposition of Aqueous Bioxalate in the Presence of Ozone](#), *J. Phys. Chem., A*, **114**:4968-4980 (2010).
- [21] Shen Y., Xu Q., Wei R., Ma J., Wang Y., [Mechanism and Dynamic Study of Reactive Red X-3B Dye Degradation by Ultrasonic-Assisted Ozone Oxidation Process](#), *Ultrason. Sonochem.*, **38**:681-692 (2017).
- [22] Xu X., Shi H., Wang D., [Study on US/O₃ Mechanism in p-Chlorophenol Decomposition](#), *J. Zhejiang Univ. Sci., B*, **6**:553 (2005).
- [23] Song S., Xia M., He Z., Ying H., Lu B., Chen J., [Degradation of p-nitrotoluene in Aqueous Solution by Ozonation Combined with Sonolysis](#), *J. Hazard. Mater* **144**:532-537 (2007).
- [24] Song S., He Z.Q., Chen J.M., [US/O₃ Combination Degradation of Aniline in Aqueous Solution](#), *Ultrason. Sonochem.*, **14**:84-88 (2007).
- [25] He Z., Zhu R., Xu X., Song S., Chen J., Xia M., [Ozonation Combined with Sonolysis for Degradation and Detoxification of m-Nitrotoluene in Aqueous Solution](#), *Ind Eng Chem Res.*, **48**:5578-5583 (2009).
- [26] Taras M.J., Greenberg A.E., Hoak R.D., Rand M.C., [Standard Methods for the Examination of Water and Wastewater](#), *American Public Health Association, Washington DC*, Section **143**: 271-274 (1974).

- [27] Marandi R., Olya M.E., Vahid B., Khosravi M., Hatami M., Kinetic Modeling of Photocatalytic Degradation of an Azo Dye Using Nano-TiO₂/Polyester, *Environ. Eng. Sci.*, **29**:957–963 (2012).
- [28] Zarei M., Salari D., Niaei A., Khataee A.R., Peroxi-Coagulation Degradation of C.I. Basic Yellow 2 Based on Carbon-PTFE and Carbon Nanotube-PTFE Electrodes as Cathode, *Electrochim. Acta*, **54**: 6651–6660 (2009).
- [29] Beltran F.J., Rivas F.J., Gimeno O., Comparison between Photocatalytic Ozonation and other Oxidation Processes for the Removal of Phenols from Water, *J. Chem. Technol. Biotechnol.*, **80**:973-984 (2005).
- [30] Yang L.P., Hu W.Y., Huang H.M., Yan B., Degradation of High Concentration Phenol by Ozonation in Combination with Ultrasonic Irradiation, *Desal. Wat. Treat.*, **21**:87-95 (2010).
- [31] Somensi C.A., Simionatto E.L., Dalmarco J.B., Gaspareto P., Radetski C.M., A Comparison between Ozonolysis and Sonolysis/Ozonolysis Treatments for the Degradation of the Cytostatic Drugs Methotrexate and Doxorubicin: Kinetic and Efficiency Approaches, *J. Environmen. Sci. Health Part A*, **47**:1543-1550 (2012).
- [32] Rajeshwar K., Osugi M., Chanmanee W., Chenthamarakshan C., Zanoni M., Kajitvichyanukul P., Krishnan-Ayer R., Heterogeneous Photocatalytic Treatment of Organic Dyes in Air and Aqueous Media, *J Photochem Photobiol C*. **9**:171-192 (2008).
- [33] Wang J., Guo B., Zhang X., Zhang Z., Han J., Wu J., Sonocatalytic Degradation of Methyl Orange in the Presence of TiO₂ Catalysts and Catalytic Activity Comparison of Rutile and anatase, *Ultrason. Sonochem.* **12**:331-337 (2005).
- [34] Ince N.H., Tezcanli G., Reactive Dyestuff Degradation by Combined Sonolysis and Ozonation, *Dyes Pigm.* **49**:145-153 (2001).
- [35] Lagha A., Ouederni A., Treatment of Dissolved Sulfides in Water by Combined Process Using Ozone and Activated Carbon, *Desal. Wat. Treat.* **53**: 1118-1125 (2015).
- [36] Little J.L., Artifacts in Trimethylsilyl Derivatization Reactions and Ways to Avoid Them, *J. Chromatogr. A*. **844**:1-22 (1999).
- [37] Khataee A.R., Safarpour M., Zarei M., Aber S., Combined Heterogeneous and Homogeneous Photodegradation of a Dye Using Immobilized TiO₂ Nanophotocatalyst and Modified Graphite Electrode with Carbon Nanotubes, *J. Mol. Catal. A: Chem.* **363**: 58– 68 (2012).