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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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 (·OH), play the main role in oxidizing organic pollutants unelectively to form carbon dioxide (CO₂), water (H₂O) 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 TiO₂, 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 (O₃), which is a stronger oxidant compared to oxygen (E°=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 O₃ rapid decomposition to yield ·OH radicals, respectively [16]. However, it has been observed that complete degradation of pollutants may not be achieved by O₃ process [17]. TiO₂-catalyzed ozonation (O₃/TiO₂) 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 TiO₂ particles [19]. The combination of ultrasonic irradiation with O₃ 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/O₃ process [20, 21]:

\[ \text{H}_2\text{O} + \text{O}_3 \rightarrow \text{H} + \cdot\text{OH} \]  
\[ \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{O}_2 + 2\cdot\text{OH} \]  
\[ \cdot\text{OH} + \cdot\text{OH} \rightarrow \cdot\text{HO}_2 \]  
\[ \cdot\text{HO}_2 \rightarrow \cdot\text{OH} + \text{O}_2 \]  
\[ \cdot\text{OH} + \cdot\text{OH} \rightarrow \text{HO}_2 \]  
\[ \text{HO}_2 \rightarrow \text{O}_3 + \text{H}_2\text{O} + \text{O}_2 \]  
\[ \text{Substance} + \text{Reactive radicals} \rightarrow \text{intermediates} \rightarrow \text{Products} \]

Many researchers have reported the removal of organic contaminants including phenolic compounds such as p-chlorophenol, p-nitrotoluene and m-nitrotoluenein 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/O₃/TiO₂ 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/TiO₂, O₃ alone, O₃/TiO₂, O₃/US and US/O₃/TiO₂ 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/O₃/TiO₂ 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±15 m²/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):

\[
\text{Power} = \frac{\text{dT}}{\text{dt}} C_p M
\]

For a sonochemical system, temperature (T) was measured versus time (t) and then from the depicted plot, \(\frac{\text{dT}}{\text{dt}}\) 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 TiO₂ (in processes which had TiO₂) was prepared. Then, the solution was treated by the chosen O₃ 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 TiO₂ 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/O₃/TiO₂ 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 (C₀–C) of DNBP at a certain process time (C) to its initial concentration (C₀). The degradation and mineralization of DNBP (40 mg/L) with US, US/TiO₂, O₃, O₃/TiO₂, US/O₃ and US/O₃/TiO₂ 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.
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 ozonalysis 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 •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/C₀)=kₚₐₚₖt, where kₚₐₚₖ is the apparent pseudo-first-order reaction rate constant. In all AOPs processes, the straight lines confirmed the proposed kinetics (Table 2). The kₚₐₚₖ 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:

\[ \text{Synergy} = \left( \frac{k_{US/O₃/TiO₂}}{k_{US/TiO₂} + k_{O₃/TiO₂}} \right) \]

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 kₚₐₚₖ for the mineralization of DNBP was determined by the same method (ln(TOC/TOC₀)=-kₚₐₚₖ), as presented in Table 2 [32]. The synergistic effect of US and O₃/TiO₂ was also noticeable for DNBP mineralization and was calculated.

Table 1: Experimental conditions of experiments.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>DNBP initial concentration (mg/L)</td>
<td>20-50</td>
</tr>
<tr>
<td>US Power density (W/mL)</td>
<td>0.09-0.4</td>
</tr>
<tr>
<td>TiO₂ dosage (mg/L)</td>
<td>30-60</td>
</tr>
<tr>
<td>O₃ concentration (mg/L)</td>
<td>2.3-60</td>
</tr>
</tbody>
</table>

Fig. 1: The experimental set-up: (1) ozone generator; (2) rotameter; (3) temperator controlled bath; (4) ultrasonic generator; (5) reactor; (6) absorption bottle.
Table 2: Pseudo-first order degradation and mineralization rate constants of DNBP in various processes.

<table>
<thead>
<tr>
<th>Treatment process</th>
<th>Degradation rate constant (min⁻¹)</th>
<th>Correlation coefficient ( R^2 )</th>
<th>Mineralization rate constant (min⁻¹)</th>
<th>Correlation coefficient ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>US</td>
<td>0.001</td>
<td>0.935</td>
<td>0.0004</td>
<td>0.970</td>
</tr>
<tr>
<td>US /TiO₂</td>
<td>0.004</td>
<td>0.977</td>
<td>0.0009</td>
<td>0.994</td>
</tr>
<tr>
<td>O₃</td>
<td>0.137</td>
<td>0.998</td>
<td>0.008</td>
<td>0.967</td>
</tr>
<tr>
<td>O₃/TiO₂</td>
<td>0.149</td>
<td>0.997</td>
<td>0.011</td>
<td>0.909</td>
</tr>
<tr>
<td>US/O₃</td>
<td>0.395</td>
<td>0.921</td>
<td>0.018</td>
<td>0.923</td>
</tr>
<tr>
<td>O₃/US/TiO₂</td>
<td>0.498</td>
<td>0.912</td>
<td>0.024</td>
<td>0.944</td>
</tr>
</tbody>
</table>

\[ [\text{DNBP}]_0 = 40 \text{ mg/L}, \text{pH} = 6.5, T = 25^\circ \text{C}, \text{O}_3 \text{ concentration} = 5.2 \text{ mg/L}, \text{US power density} = 0.4 \text{ W/mL and TiO}_2 \text{ dosage} = 50 \text{ mg/L} \]

Fig. 2: (a) Degradation curves of DNBP and (b) removal of TOC by various oxidation processes. Experimental conditions: \( \text{pH} = 6.5, 50 \text{ mg/L TiO}_2, \text{C}_0 = 40 \text{ mg/L, ozone gas concentration} = 5.2 \text{ mg/L and US power density} = 0.4 \text{ W/mL} \)

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/O₃/TiO₂ process. Experimental conditions: 50 mg/L TiO₂, 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/O₃/TiO₂ process. Experimental conditions: pH = 6.5, 50 mg/L TiO₂, C₀ = 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/O₃/TiO₂ process. Experimental conditions: pH = 6.5, 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 O$_3$/US/TiO$_2$ process.**

<table>
<thead>
<tr>
<th>Operational parameters and amounts</th>
<th>Degradation rate constant (min$^{-1}$)</th>
<th>Correlation coefficient ($R^2$)</th>
<th>Mineralization rate constant (min$^{-1}$)</th>
<th>Correlation coefficient ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DNP concentration (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.817</td>
<td>0.931</td>
<td>0.032</td>
<td>0.907</td>
</tr>
<tr>
<td>30</td>
<td>0.77</td>
<td>0.903</td>
<td>0.027</td>
<td>0.942</td>
</tr>
<tr>
<td>40</td>
<td>0.498</td>
<td>0.912</td>
<td>0.024</td>
<td>0.944</td>
</tr>
<tr>
<td>50</td>
<td>0.269</td>
<td>0.965</td>
<td>0.02</td>
<td>0.932</td>
</tr>
<tr>
<td>US density (W/mL)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.09</td>
<td>0.211</td>
<td>0.987</td>
<td>0.013</td>
<td>0.969</td>
</tr>
<tr>
<td>0.25</td>
<td>0.273</td>
<td>0.98</td>
<td>0.019</td>
<td>0.948</td>
</tr>
<tr>
<td>0.4</td>
<td>0.498</td>
<td>0.912</td>
<td>0.024</td>
<td>0.944</td>
</tr>
<tr>
<td>TiO$_2$ dosage (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.258</td>
<td>0.995</td>
<td>0.019</td>
<td>0.939</td>
</tr>
<tr>
<td>40</td>
<td>0.277</td>
<td>0.995</td>
<td>0.021</td>
<td>0.947</td>
</tr>
<tr>
<td>50</td>
<td>0.498</td>
<td>0.912</td>
<td>0.024</td>
<td>0.944</td>
</tr>
<tr>
<td>60</td>
<td>0.507</td>
<td>0.919</td>
<td>0.025</td>
<td>0.912</td>
</tr>
<tr>
<td>O$_3$ concentration (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>0.154</td>
<td>0.999</td>
<td>0.018</td>
<td>0.932</td>
</tr>
<tr>
<td>5.2</td>
<td>0.498</td>
<td>0.912</td>
<td>0.024</td>
<td>0.944</td>
</tr>
<tr>
<td>6.8</td>
<td>0.688</td>
<td>0.873</td>
<td>0.027</td>
<td>0.947</td>
</tr>
</tbody>
</table>

Amount of operational parameters, except the conditions mentioned above: [DNP]$_0$ = 40 mg/L, pH = 6.5, $T = 25^\circ$C, O$_3$ concentration = 5.2 mg/L, US power density = 0.4 W/mL and TiO$_2$ dosage = 50 mg/L.

**Table 4: Identified intermediates during US/O$_3$/TiO$_2$ process.**

<table>
<thead>
<tr>
<th>Intermediates</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dinitro catechol</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Nitrophenol</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Maleic acid</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Oxalic acid</td>
<td><img src="image" alt="Structure" /></td>
</tr>
</tbody>
</table>

**Reusability of the catalyst and Mineralization of a real wastewater by US/O$_3$/TiO$_2$ 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 DNP 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 O$_3$/US/TiO$_2$ process.

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