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Application of green iron-based persulfate/O_3 activator on explosive mineralization from aqueous solution

Masoumeh Khatebasreh[a,b], Fahimeh Teimouri[a,*], Mohammad Hassan Ehrampoush[a], Aliasghar Ebrahimi[a], Mohsen Sadani[c]

[a]*Environmental Science and Technology Research Center, Department of Environmental Health Engineering, School of Public Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran, emails: f.teimouri@ssu.ac.ir (F. Teimouri), Khatebasreh_4@yahoo.com (M. Khatebasreh), ehrampoush@yahoo.com (M.H. Ehrampoush), ebrahimi20007@gmail.co (A. Ebrahimi)*
[b]*Student Research Committee, Shahid Sadoughi University of Medical Sciences, Yazd, Iran*
[c]*Department of Environmental Health Engineering, School of Public Health and Safety, Shahid Beheshti University of Medical Sciences, Tehran, Iran, email: m.sadani82@gmail.com*

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ABSTRACT

Energetic compounds are widely used in various activities, including military exercises and conflicts. Researchers recently proved that these compounds could persuade apoptosis through DNA damage, endoplasmic reticulum stress, and mitochondrial dysfunction in Hep3B and HepG2 cells. This study investigated the possibility of potassium ferrate as an eco-friendly and simultaneous activator (PS/PF/O_3) for explosive degradation from an aqueous solution. Taguchi design method was used for evaluating the effect of different operational parameters. chemical oxygen demand (COD) and total organic carbon (TOC) removals were considered responses of the study experiments by analysis of variance (ANOVA). The optimum condition was achieved at neutral pH value and an oxidant dose of 19 mM; 40 mg/L of 2,4,6-trinitrotoluene within 60 min responded to almost 89.3% of COD and 75.7% of TOC removal by PS/PF/O_3 process. In the mentioned condition, 2,4,6-trinitrobenzaldehyde, 2,4,6-trinitrobenzoic acid, and 1,3,5-trinitrobenzene were the main intermediates detected by liquid chromatography–mass spectrometry analysis. Also, this reaction chain was subsequently continued, and nitrate ions were identified as a key factor for mineralization. Bioassay test also demonstrated a considerable reduction in toxicity after each process. The dispersion test of *Daphnia magna* assay on treated red-water ranked as follows: stock solution (high toxicity) >> PF/O_3 effluent > PS/PF/O_3 (low toxicity). Degradation of 2,4,6-trinitrotoluene was in accordance with the pseudo-first-order kinetic model ($R^2 = 0.98$). It can be concluded that potassium ferrate makes the PS/O_3 process a reliable technique for explosive mineralization (as a green iron-based activator).

Keywords: Nitroaromatic; 2,4,6-Trinitrotoluene; Advanced oxidation process; Persulfate; Toxicity; Intermediate

1. Introduction

The ever-increasing production of energetic waste compounds in various activities, including military exercises and conflicts, has become a widespread problem worldwide [1]. This trend is probably continuing with increasing groundwater and soil contamination from 2,4,6-trinitrotoluene (TNT). Reliable evidence about extensive contamination of these sources with TNT is also reported [2,3]. However, there are significant adverse effects on the environment from chemicals and toxic compounds of unexploded ordnance (UXO) and their by-products, especially in industrial processes and civilian purposes [4,5]. In addition, the

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* Corresponding author.

accumulation of these compounds leads to a genetic mutation in humans, animals, microorganisms, and algae.

In some cases, they also have detrimental effects, such as increasing or decreasing white blood cells, respiratory and heart problems, and chronic gastrointestinal complaints [6,7]. Researchers recently demonstrated that explosives such as TNT can persuade apoptosis through DNA damage, endoplasmic reticulum stress, and mitochondrial dysfunction in Hep3B and HepG2 cells [8,9]. Various cost-intensive methods have been determined for TNT degradation [10–13]. Red water is the wastewater of TNT manufacturers. Among the numerous 2,4,6-trinitrotoluene red water treatment procedures, advanced oxidation processes (AOPs) are considered an excellent technology due to their low cost and high efficiency.

On the other hand, potassium ferrate (PF) is a green pollution-free oxidant. As an environmentally friendly oxidant, potassium ferrate (PF) is an intense oxidant for degrading various inorganic and organic compounds [1,14]. So, it attracted some attention in the wastewater treatment process. The reduction/oxidation potential of ferrate ions (FeO_4^{2-}) in an acidic condition is 2.20 V, and in an alkaline environment, it is 0.72 V, as indicated in Eqs. (1) and (2). It should be noted that under acidic conditions, the oxidizing power of potassium ferrate is significantly stronger than other regularly used oxidants, including hydrogen peroxide (1.36 V), permanganate (1.15 V), and ozone (2.07 V) [15].

$$H_3Fe^{VI}O_4 + H^+ + H_2Fe^{VI}O_4 \qquad pK_a = 1.6 \pm 0.2 \tag{1}$$

$$H_2Fe^{VI}O_4 + H + HFe^{VI}O_4^- \qquad pK_a = 3.5 \tag{2}$$

In addition, no adverse or toxic products are produced during the potassium ferrate oxidation process, and the generation of ferric ion (Fe^{3+}) is considered a great flocculant agent that can support more removal of remaining contaminants and increase the treatment [16]. Given these excellent features, potassium ferrate is a well-known eco-friendly oxidant, and its capability for the treatment of various wastewater has been extensively investigated.

For instance, some studies indicated that potassium ferrate could reduce sludge water content because it can effectively disintegrate sludge flocs and promote the dissolution of particulate organic matter due to the excellent oxidation of Fe(VI) [17]. During the disintegration process, sludge was minimized simultaneously. Furthermore, increasing the content of soluble organic matter is useful for anaerobic sludge fermentation, and more fermentation products are produced [18]. Degradation of pollutants in sewage is always difficult, and PF can also degrade the minerals of these anti-inflammatory substances [19].

Recently, studies related to treating polluted water or wastewater by sulfate radical-based AOPs have been enhanced. Persulfate anion (PS) is consumed as precursors of radical sulfate formation [18–20]. This anion can be activated in various ways to generate sulfate radicals. Besides, PS displays more application in sulfate radical production due to low harm, simple handling, and low expense [19].

So, it can be concluded that potassium ferrate has multipurpose roles in the wastewater treatment processes, such as mineralization and remediation of pollutants. This study investigated two kinds of AOPs aspects in the treatment of redwater: green iron-based persulfate and a combination of ozone and persulfate (PS). Hence, these processes contributed to degrading 2,4,6-trinitrotoluene, including the free radical production by PS (1) and PF/O_3 (2). In other words, this study mainly aimed to use advanced oxidation processes as ferrate reactions (as a green oxidant) for activation of PS/O_3 by an Integrated Green Oxidation Process (IGOP).

2. Materials and methods

2.1. Reagents and materials

2,4,6-trinitrotoluene (TNT) ($C_3H_5N_3O_6$) (CAS number: 95-14-7) crystalline was obtained from a local industry producing explosive materials (purity > 95%). Sodium persulfate (PS) (CAS number: 7727-54-0) was purchased from Sigma-Aldrich Company. Potassium ferrate (PF) (CAS number: 5412-47-2) was provided from Isfahan Science and Technology Town (ISTT).

2.2. Experimental procedure (design of experiments)

Experiments of the process were optimized and designed with Minitab Software (version 16) and the Taguchi method. The range of parameters includes pH (4–10), time (15–60 min), oxidant dose as millimolar (5–25 mM), and TNT concentration (10–100 mg/L).

According to Taguchi's design, 32 experiments were conducted (16 setups for $PS/PF/O_3$ and 16 set up for PF/O_3, respectively). Due to the low solubility of TNT, the stock solution was prepared by solving it in ethanol. The ozone gas was injected into a Plexiglas containing 1,000 mL of deionized water (0.5 mg/L). The injection was continuously performed through a ceramic diffuser from the bottom (Fig. 1).

Also, 0.1 M of sulfuric acid and 0.1 N sodium hydroxide were used to adjust the solution pH [20].

2.3. Analysis

High-performance liquid chromatography (HPLC) with a UV detector (KNAUER, Germany) was used to quantify TNT residual concentration from the TNT calibration curve. The HPLC operated with a reverse phase C_{18} column (3.5 µm, 4.6 × 250 mm). The mobile phase was consisted of 70/30 of methanol/water with a wavelength of 520 nm, at a flow rate of 0.1 mL/min.

Liquid chromatography–mass spectrometry (LC–MS) instrument (LCMS-8045) was used for TNT by-product degradation process detection. The total organic carbon (TOC) solution was also measured to evaluate TNT mineralization in PS/O_3 process using a TOC analyzer (Shimadzu Co.). The HACH method measured chemical oxygen demand (COD) and nitrate ions by 5220-D and 4500-B colorimetric methods.

2.4. Bioassay test

Daphnia magna were supplied from laboratory cultures maintained at Behbahan University. Culturing of organisms was followed by standard procedures (EPA 2002). *D. magna* was maintained at 24°C ± 1°C with an 18:6 h light: dark photoperiod and was less than 24-h old in the experiments. The tests were carried out at 24°C and a contact period under a photoperiod of 8/16 (dark/light) incubator. A phytotoxicity modified method was performed to conduct the acute *D. magna* test. 100 mL of effluent concentrations and control were introduced to the beaker. After that, ten *D. magna* neonates were slowly added to the solutions for 96-h in a static test to calculate the acute lethality test.

After 24, 48, 72, and 96 h exposure, the mobile and immobile (abnormal behavior or appearance) specimens were counted for each effluent. All bioassay tests were done in triplicate, and all data experiments were statistically analyzed by SPSS software. The half-maximal effective concentration as EC_{50} values were computed using the probit method for *D. magna*. Eventually, mortality percentages were calculated after being exposed for 24–96 h.

3. Result and discussion

3.1. Optimization of the process

The Taguchi method applies fractional factorial S/N (Signal to Noise) test designs called orthogonal arrays that reduce the number of experiments. To determine the most significant parameters affecting COD and TOC removal, variance (ANOVA) analysis was used. In this way, a standard L16 orthogonal array analysis was established to define the optimized amount of the controllable factors by which favorable efficiencies of the responses (estimated effects on the removal performance indicators) (COD, TOC, and NO_3 removals) were achievable. The second-order polynomial response model was used to indicate the interaction among the four factors (pH, time, TNT concentration, and oxidant dose) and the three responses (estimated effects on the removal performance indicators) (COD, TOC, and NO_3 removals). The correlation coefficient of 0.9 indicated high validity of the obtained models for removing COD, TOC, and NO_3. Hence, for COD and TOC removal, a beneficent adoption was found between the experimental and predicted values of the responses [21].

According to the results, the pH was the most important (39%), and the TNT concentration was the least important factor (8%) for these AOPs systems. Also, the highest contribution percentage for all the samples occurred in the following order: pH > oxidant > reaction time > TNT concentration. Table 1 and Fig. 2 summarize the optimum conditions for TNT removal using the present process.

3.2. Effect of parameters by PS/PF/O_3 process

In this study, applications of chemical oxidants in red-water treatment encompass potassium ferrate, ozone, and persulfate. Advanced oxidation processes such as ferrate-type reactions noticeably implicate the generation of hydroxyl radical, a non-selective and strong oxidant that can be produced by multitudinous combinations of advanced oxidation processes reagents, including PF in combinations with O_3 and PS for the destruction of TNT pollutants.

Table 1
Optimum condition as S/N ratio results

Factor	Level description	Level	Contribution
pH	3	3	15.59
Oxidant (mM)	3	3	3.09
Reaction time (min)	3	3	0.80
TNT (mg/L)	3	3	0.63

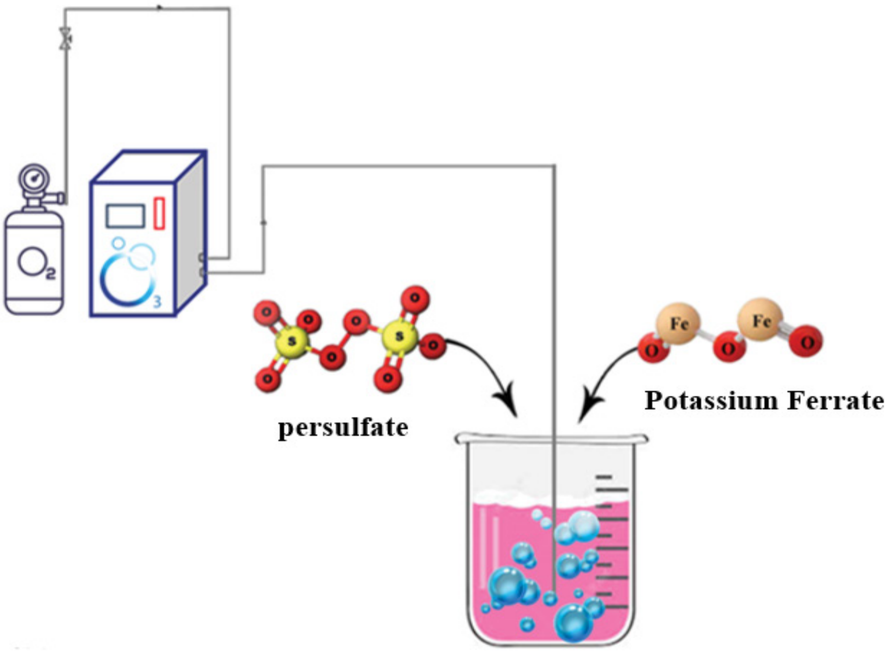

Fig. 1. A schematic of experimental procedure.

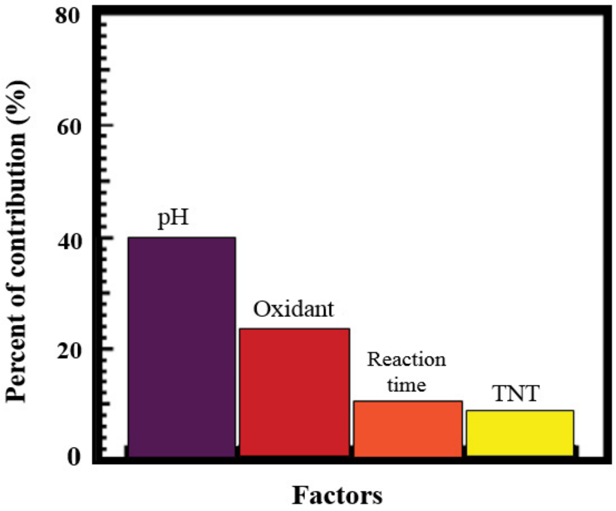

Fig. 2. The contribution of each factor on TNT degradation.

Table 2
The comparison of two processes for TNT removal

Process	k_1 (min^{-1})	R^2
PF/PS/O_3	0.0713 ± 0.0016	0.98
PF/O_3	0.0118 ± 0.0012	0.96

In this way, the solution pH is considered an important parameter in chemical reactions [22,23]. As shown (Fig. 3a), the efficiency of TNT degradation in alkaline and acidic conditions sharply dropped and an obvious TNT degradation efficiency reached a neutral pH value. It was found that the degradation process of TNT was undesirable in acidic conditions.

This result is explained by a dominant sulfate radical species theory in the reaction, which is directly relevant to solution pH [20,24]. On the other hand, the proposed document indicates that $SO_4^{-\bullet}$ is probably steady throughout the acidic condition. Moreover, in the acidic range, the removal rate is moderately owning to the H^+ ion scavenging effects of the radicals $^\bullet OH$ and $SO_4^{-\bullet}$ [24]. It should be noted here that advanced oxidation processes, including ferrate-type reactions, are confined by low pH situations (4 > pH). However, in the attendance of iron ligands, pH can be extended to the neutral condition. Howbeit ozonation is an effective process in higher pH value for generation of hydroxyl radical; persulfate decomposes at alkaline conditions. In this process, the reduction of TNT degradation at higher pH (>8) is likely because of the lower reactivity of the ferrate complex, which generates through the alkalinity reaction in combination with persulfate. What's more, in this condition, the decrease in TNT degradation is probably due to the transformation of sulfate radical (SR) to HO [24].

Therefore, the proportion of SR decreases dramatically in higher values of pH. PS in forms of SO_4^{2-} and HSO_4^- and

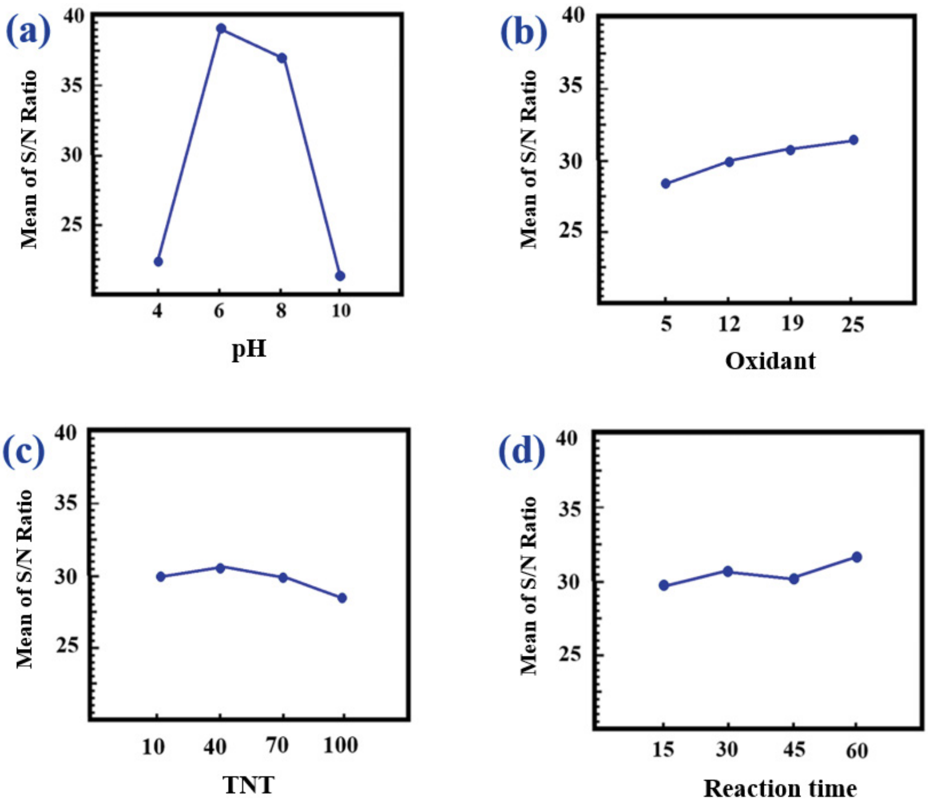

Fig. 3. Main effects plot for S/N ratios on TNT removal in PS/PF/O_3 process (a) pH, (b) oxidant dosage, (c) TNT dosage and (d) reaction time.

potassium ferrate with negative surface charge in an alkaline condition caused an electrostatic repulsion between activator and oxidant, resulting in reduced free radical productions.

Potassium ferrate has a negative surface charge in an alkaline environment, which can cause electrostatic repulsion among oxidant and activator, thus reducing the production of free radicals. On the other hand, there is a repulsion among the surface activator and 2,4,6-trinitrotoluene in an alkaline environment as 2,4,6-trinitrotoluene had a negative charge according to the attendance of potassium ferrate [25]. Additionally, it is important to notice that pH values lower than the pKa value can cause a higher degradation rate of TNT.

PS concentration was the other operating parameter in the present study which was used as the radical sulfate precursor. To find the optimum amount of the persulphate in the PS/PF/O_3 process, various concentrations of PS (5, 12, 19, and 25 mM) were added to the TNT-containing solution. The results showed that TNT degradation was also affected by PS concentration, and increasing the PS concentration from 5 to 25 mM led to the increase of removal efficiency from about 78% to 96% at 60 min reaction time. As shown in Fig. 3b, the removal efficiency of TNT at PS concentration of 19 mM is very close to the removal efficiency at PS concentration of 25 mM. Therefore, it can be concluded that further increase of PS doesn't enhance the process performance, and also it may lead to the reduction of removal efficiency. This is also due to the higher generation of oxidizing radical and self-scavenging which takes place by radical species. This is in accordance with the findings of other researchers. Chen et al. [26] indicated that the destruction rate of phenol as a target contaminant decreased at a high concentration of PS. This may be attributed to the oxidant inhibition effect of oxidants on reactive radicals and the formation of less reactive species such as $SO_4^{\bullet-}$ and $HO_2^{\bullet}$ [Eqs. (3)–(4)].

$$HSO_5^- + {}^{\bullet}OH \rightarrow SO_5^{\bullet-} + OH^- \qquad (3)$$

$$HSO_5^- + SO_4^{\bullet-} \rightarrow SO_4^{2-} + H^+ \qquad (4)$$

Regarding the previous discussion of the pH effect, it can be mentioned that an increase in PS concentration led to a rise in the concentration of protons in the solution, and it consequently increased the effect of scavenging through excessive H^+.

So, it can be proposed that increasing in PS concentration enhanced the amount of proton in the process. Consequently, it can increase the effect of scavenging through exceeding H^+.

The presence of potassium ferrate (as Fe(III)) decomposed PS to $SO_4^{\bullet-}$ [Eq. (5)] and generated Fe(II) was an activator agent for PS to produce sulfate radicals throughout the process based on Eq. (6) [27]. Afterward, in order to have Fe(II) and $SO_4^{\bullet-}$, ferrate reacts with HSO_4^-.

$$Fe(III) + HSO_5^- \rightarrow Fe(II) + SO_5^{\bullet-} + H^+ \qquad (5)$$

$$Fe(II) + HSO_5^- \rightarrow Fe(III) + SO_4^{\bullet-} + OH^- \qquad (6)$$

In previous studies, the presence of $SO_4^{\bullet-}$ on the activator surface was attributed to attaching for producing oxygen and sulfate radical [Eq. (7)]. Besides, $SO_4^{\bullet-}$ production during the process is probably due to the connection of $SO_5^{\bullet-}$ with O_3, leading to accelerating TNT degradation. As a result, 19 mM was selected as a suitable PS concentration for reducing the cost of this process for TNT degradation.

$$Fe(III) + HSO_5 + O_3 \rightarrow Fe(II) + SO_4^{\bullet} + 2O_2 \qquad (7)$$

PF concentration was one of the other investigated parameters in the PS/PF/O_3 process. Potassium ferrate demonstrated a tremendous function for simultaneous PS/O_3 activation. Investigating the effect of PF concentration can support the preferable understanding of the interaction between O_3 and PS. Several concentrations of PF (5, 12, 19, and 25 mM) were selected to evaluate the PS/PF/O_3 system in the condition shown in Fig. 3c. In the presence of PF, 2,4,6-trinitrotoluene degradation efficiency was 98.9%; Which was significant for PS or ozone activation. This result is a piece of evidence for a synergistic effect of PS/O_3. This result is a document of a synergistic effect of PS/O_3. In fact, in attendance of ozone, persulfate can activate to produce sulfate radicals. Finally, ozone decomposition leads to hydroxyl radical generation according to [Eqs. (8)–(9)] [28].

$$SO_4^{\bullet-} + O_3 \rightarrow 3OH^- \qquad (8)$$

$$SO_4^{\bullet-} + OH \rightarrow HSO_5 \qquad (9)$$

Moreover, the reaction of gas oxidants in the presence of potassium ferrate with liquid oxidants resulted in the production of a large number of hydroxyl and sulfate radicals, which support the degradation of organic compounds. However, the presence of PF in PS/O_3 dramatically increased 2,4,6-trinitrotoluene degradation. The 2,4,6-trinitrotoluene removal was 67.8%, 88.9%, 98.9% and 99.8% respectively for 5, 12, 19 and 25 mM of PF. The attendance of potassium ferrate in PS/O_3 significantly enhanced 2,4,6-trinitrotoluene degradation. Two causes may describe remarkable removal. First, the tendency of simultaneous PS/O_3 to be activated by ferrate. Second, an increase in ferrate potassium concentration provided more free radicals for degradation of 2,4,6-trinitrotoluene. In other words, this is the catalytic activity procedure of potassium ferrate for activations of PS/O_3 and interaction of persulfate with ozone in radical reaction.

Fig. 3d displays the performances of these optimized conditions during degradation time. As expected, an increase in reaction time increased removal efficiencies in PS:PF/O_3 process. In this way, based on attributed to the high decomposition of the oxidant, the presence of iron ion and hydroxyl radical was enhanced with increasing the reaction time. The PS/PF/O_3 was an impressive treatment method for TNT decomposition since removal efficiency dramatically increased during 60 min of reaction time.

3.3. *Effect of parameters (PF/O_3 process)*

The pH solution is a critical parameter that affects the performance of the PF/O_3 process in the degradation of TNT due to its role in the inspection of the iron species' activity and free radicals.

Hence, the oxidation of Fe^{3+} to Fe^{2+} during this process has also been affected by pH. Four levels of pH (4.0, 6.0, 8.0, and 10) were considered to evaluate the effect of pH. Fig. 4a displays the effect of pH on TNT removal in the PF/O_3 process under the experiment condition. As can be seen, with an increase in pH, degradation of the pollutant was sharply raised. The best efficiency of PF/O_3 was shown in pH = 6.0 and pH = 8.0 with 87.1% and 86.2% removal efficiency.

It is worth emphasizing that the above condition increased the release of ferrous ions from the potassium ferrate resulting in more activation of OH^-. In the existence of high proton, ferrous ions were provided for ozone activation to generate hydroxyl radicals. Regardless, this phenomenon can be ipso facto a removal mechanism, but due to this fact, it can be consummated that generated flocs are not enough [29] to degrade TNT.

As can be interpreted, that neutral pH value results in a slow increase in TNT removal efficiency. Moreover, hydroxyl radicals are stronger in acidic conditions than in alkaline ones. Ozone disintegration is occurred at pH = 4.0 for generating the later oxidant such as hydroxyl radical.

Fe ions in the ferrate anions (e.g., $HFeO_4^-$ and FeO_4^{2-}) (Fe(OH) and $Fe(OH)_4$) may present at high pH values; this is most likely due to the deficiency of coagulation abilities and oxidizing factor for decomposition of ozone and TNT degradation [25,26,30].

In the PF/O_3 process at neutral pH value condition, dominant oxidant agents were $HO^{\bullet}$ and O_3, which participate directly in the TNT degradation procedure. Therefore, this range was chosen as an optimum pH for PF/O_3 system.

From Fig. 4 it could be understood that in pH 6–8, a high TNT degradation was obtained. This is despite the fact that negligible removal efficiency was shown in an entirely acidic and alkaline situation [31,32].

As can be seen, with the increase of PF dosage from 5 to 19 mM, the efficiency of TNT removal increased. Howbeit results indicated that a pronounced reduction of removal efficiency was found with the increase of PF dosage (>25 mM).

The redox route of Fe(III)/Fe(II) creates a synergistic effect in the previous system, which presents an excellent rate of TNT degradation. This result displayed that the decomposition of ozone is affected by non-dissociated hydroxyl groups from potassium ferrate oxidants.

Indeed, in the presence of potassium ferrate, ozone reacts with the OH group. Throughout the pathway, hydroxyl radicals and $O_3^{\bullet-}$ will be produced. The reactions of free radicals result in the formation of superoxide radicals and oxygen. However, a significant increase in TNT degradation will occur.

Furthermore, the excessive PF dosage can be a negative effect on TNT removal efficiency. A likely assumed cause for this function could be the reaction of radicals with each other in lieu of radical-TNT reaction, according to Eq. (10)

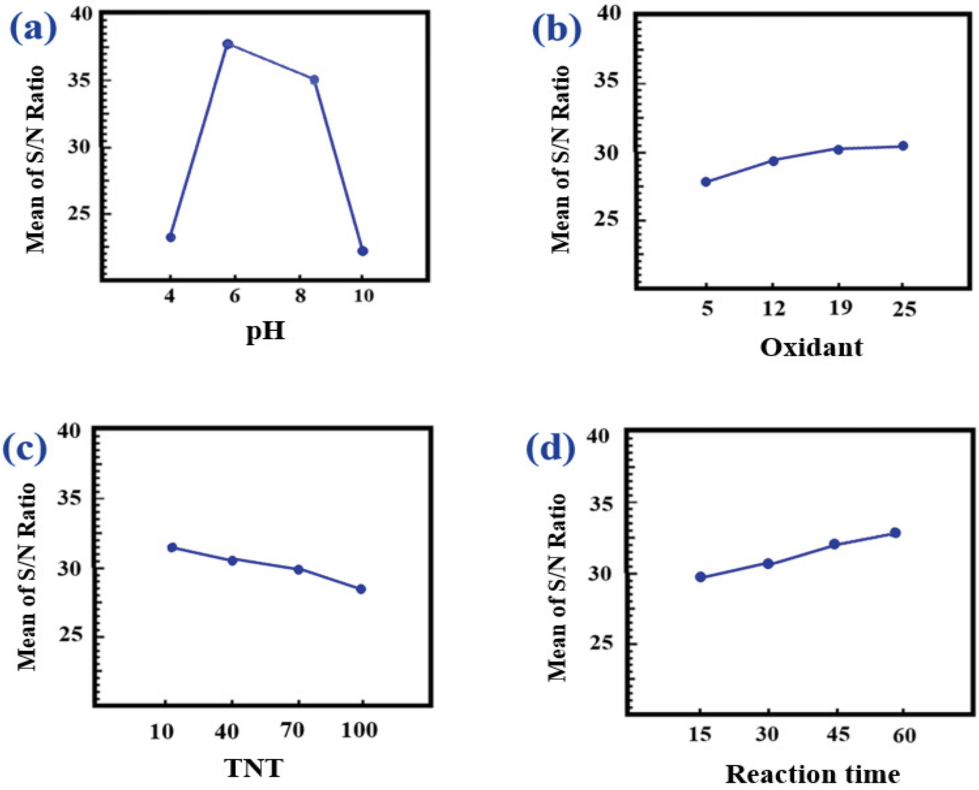

Fig. 4. Main effects plot for S/N ratios on TNT removal in PF/O_3 process (a) the effect of pH, (b) oxidant dosage, (c) TNT dosage and (d) reaction time.

[22,33]. Therefore, the PF dosage of 19 mM was the optimum condition with 92.1% removal efficiency. This result is evidence of a synergistic effect of persulfate and ozone.

$$FeO_4^{2-} + OH \rightarrow Fe_4 \tag{10}$$

Ferrous ions can activate this oxidant as an activator to produce free radicals [29,34]. Ferrous ions are used to activate O_3, which forms an iron reagent in combination with the latter oxidant.

$$Fe^{2+} + S_2O_8^{-} \rightarrow SO_4^{2-} + Fe^{3+} + SO_4^{2-} \tag{11}$$

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \tag{12}$$

$$FeO^{2+} + H_2O \rightarrow 2HO^{\bullet} + Fe^{3+} + OH^{-} \tag{13}$$

Ferrous ion reacts with generated hydroxide ion and produces metal hydroxide that can precipitate organic and inorganic pollutants [Eq. (14)]. However, ferrous ion acts as an activator in the presence of an oxidant and plays the role of coagulant agent. The combination of this oxidant can dramatically increase the performance of the process for degrading the 2,4,6-trinitrotoluene.

$$FeO_4^{2-} + OH \rightarrow Fe_4 \tag{14}$$

A slight increase in the PF dosage from 12 to 19 mM caused a significant increase in removal efficiency from about 69% to 92%.

However, at a concentration of 5 and 25 mM, removal efficiencies decreased about 61% and 78%, respectively.

The high iron ions generation affects the reaction of $OH^{\bullet}$ and O_3 with TNT. It can be realized that at a higher concentration of iron ions, FeO^{2+} can be oxidized to ferric ions in the production of free radicals under neutral pH conditions [Eq. (15)] [35]. Therefore, 19 mM was the optimum PF dosage for PF/O_3 process.

$$FeO_2^{+} + Fe(II) \rightarrow Fe(III) \tag{15}$$

As expected, increasing the reaction time increased the removal efficiency in both systems. As the reaction time increased, the amounts of ferrous ions were increased due to the high disintegration of the oxidant reagents [35,36]. As can be seen, the PF/O_3 treatment method was an effective system for TNT degradation since removal efficiency dramatically enhanced during 60 min of reaction time.

The amounts of ferrous ions were increased with increasing the reaction time resulting in high decomposition of the oxidant [35,36]. As can be seen, the PF/O_3 process was an efficient process for degradation of TNT since removal efficiency significantly increased during 60 min of reaction time.

3.4. Feasibility of TNT mineralization

In order to identify the trend of TNT degradation, mineralization was evaluated by COD and TOC removal under optimal operating conditions, and the results are depicted in Fig. 5a.

The results endorsed TNT removal efficiency in the first process was 89.3% of COD and 82.1% of TOC. The PF/O_3 process's optimal operating condition also contributed to the almost 77.2% and 75.7% COD and TOC removal, respectively.

The preferable TOC removal efficiency of the PS/PF/O_3 demonstrates that almost 82% of the TNT has degraded inorganic substances such as CO_2. After treatment by PS/PF/O_3 system, TOC removal was increased to raise COD removal. Based on these results, it can be concluded that higher TNT mineralization rates may be related to the production of more oxidative species produced in the PS/PF/O_3 process. Moreover, leaching iron ions results in more function in this system. These results represented the synergistic effect of simultaneous attendance of PF on TNT mineralization.

Chen et al. investigated the mineralization of TNT in the UV/O_3 process. They reported that an approximate 50% TOC decreased after a reaction time of 24 h, while TNT was degraded entirely, indicating that 50% of the TNT was still as other forms of organic compounds. It has been reported that only 22% TOC reduction efficiency of TNT in 30 min reaction time using EC/persulphate salt. In another study, catalytic ozonation using H_2O_2 showed that after 32 min of reaction time, almost a low percent of TOC was removed [37].

The evolution of nitrogen ions was also monitored in TNT decomposition using PS/PF/O_3 and PF/O_3 processes. In this way, NO_3 was measured during TNT oxidation. The results of nitrate ion measurement are presented in Fig. 5b.

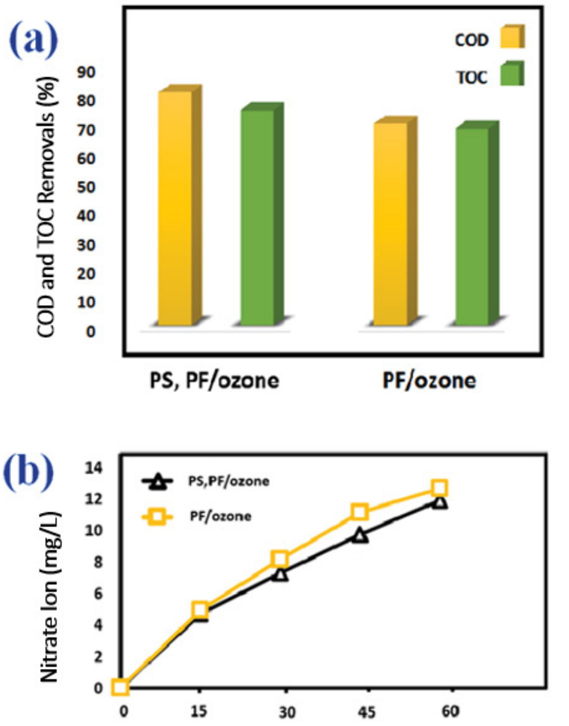

Fig. 5. Key factors for process control: (a) COD and TOC removals and (b) nitrate ions (pH = neutral, oxidant = 19 mM (persulfate/potassium ferrate), TNT = 40 mg/L as optimum condition).

LC–MS spectrum analysis (Fig. 6) was used to determine the by-products of TNT mineralization. As can be seen, depicted an identified and proposed reaction of intermediates (Fig. 7). It is substantial to mention that this analysis was in the condition of 82.1% TOC removal.

In general, the degradation mechanism of TNT may be considered as three steps, methyl group oxidation, decarboxylation, and mineralization of nitro-groups. The principal diversity between 2,4,6-trinitrotoluene and its formatives is based on the positioning of nitro groups on the benzene

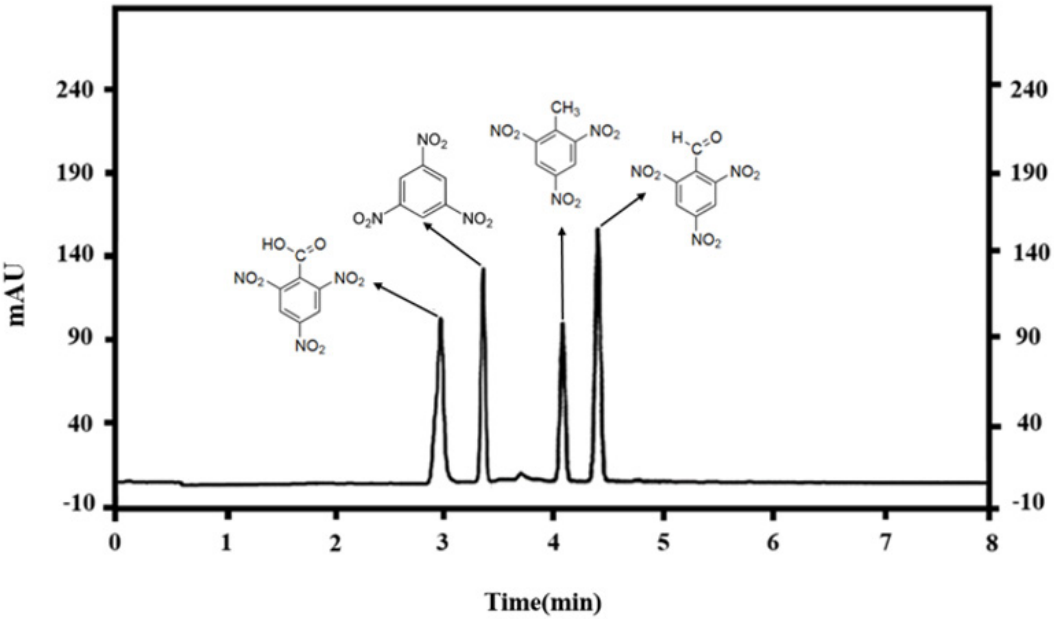

Fig. 6. LC–MS chromatograms for TNT degradation by PF/PS/O_3 system in optimum condition.

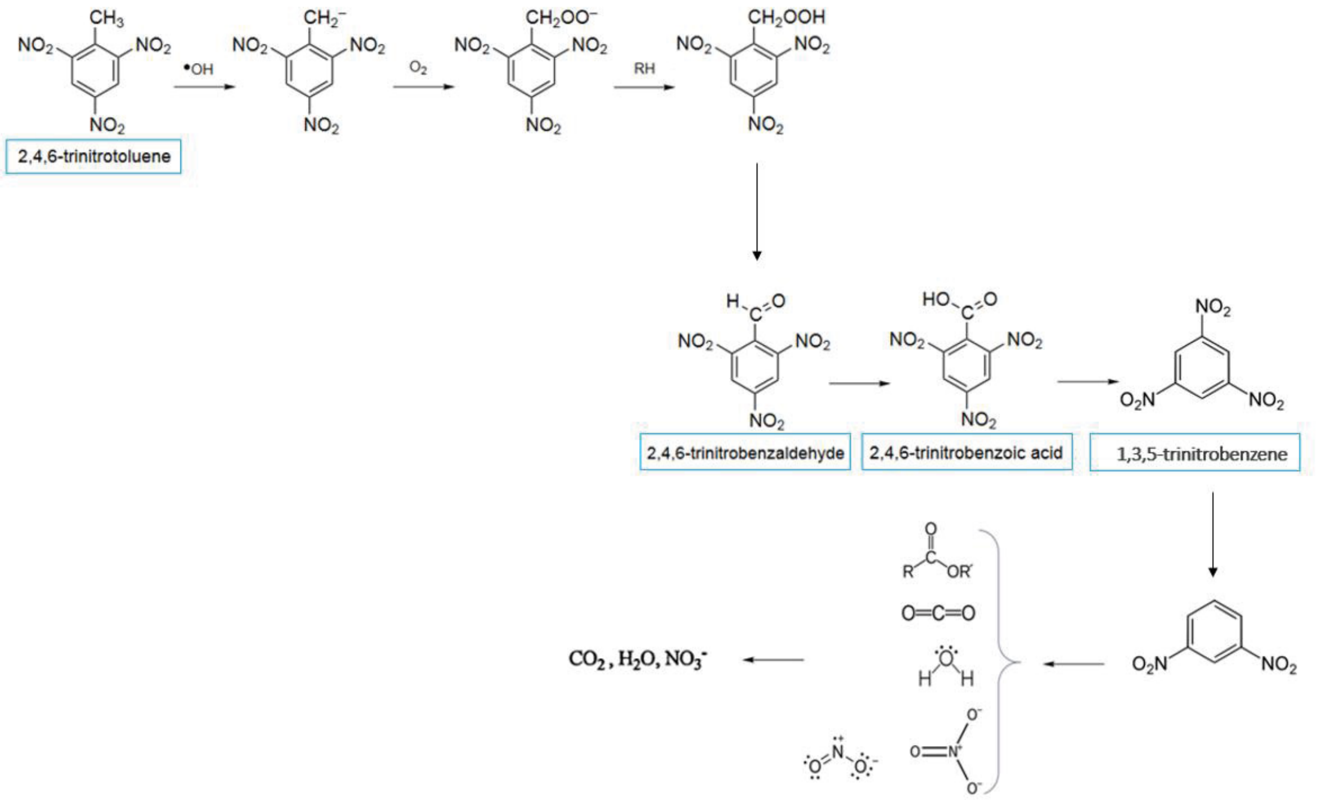

Fig. 7. Proposed reaction of TNT degradation (PF/PS/O_3) in optimum condition.

ring. Oxidation and reduction of 2,4,6-trinitrotoluene functional groups are the main reactions of TNT, which are replaced in the benzene ring. [38].

In the present study, the methyl group of TNT oxidized to 2,4,6-trinitrobenzaldehyde, which proceeded oxidation into 2,4,6-trinitrobenzoic acid. Subsequently, decarboxylation of aromatic acid to 1,3,5-trinitrobenzene. A similar mechanism was suggested by Chen et al. They used UV/O_3 and O_3 to mineralize TNT. It is notable that oxidative degradation of TNT results in a 1,3,5-trinitrobenzene by-product [39].

Finally, aromatic ring opening occurs for a molecule to form carboxylic acids with short chains. Methyl group in 2,4,6-trinitrotoluene could be oxidized to the carboxyl group, under the influence of oxidative effects, that it will be removed in the process of decarboxylation, forming 1,3,5-trinitrobenzene [39]. Also, TNT may undergo some reactions that lead to the formation of 2,4,6-trinitrobenzoic acid and 1,3,5-trinitrobenzene [40,41].

Further oxidation occurred in the mineralization of organic compounds and the formation of carbon dioxide, water, and inorganic nitrogen species. In this step, nitrogen evolution could occur, and nitrate and nitrite ions can be mineral products. The reaction stoichiometry could be defined as follows:

Qiao et al. [42] observed two substances resulting from the polymerization of nitrobenzene degradation by the ozone/persulfate oxidation process. According to TNT's carbon and nitrogen mineralization results (78% C-mineralization and 89% N-mineralization), further oxidation would lead to ring-opening and, consequently, mineralization of organic by-products.

3.5. Kinetic reactions of PS/PF/O_3 and PF/O_3

The kinetic reaction is well known as one of the most important parameters in operation conditions. The results of kinetic reactions are depicted in Fig. 8a. As expected, an increase in reaction time enhanced the efficiency of TNT removal in these processes. It was clear that lower TNT concentration was sharply destructed due to the high free radicals in comparison with low numbers of TNT molecules.

The reaction rate constant of PF/PS/O_3 was 0.0713 min^{-1}. According to the Table 2 results, it should be concluded that PF/PS/O_3 can degrade more TNT at 60 min reaction time, whenever PF/O_3 requires more time to proceed with this process.

In order to determine the degradation rate of TNT, the first-order kinetic model was evaluated by linear forms using Eq. (16):

$$\ln\left(\frac{C_0}{C_t}\right) = kt \tag{16}$$

where C_t and C_0 are applied concentrations of the TNT in the solution before and after the reaction, respectively, and k is the pseudo-first-order reaction rate constant (min^{-1}). Fig. 8b demonstrates the plot of [Eq. (16)] for TNT degradation for these processes.

The reaction rate constant values of TNT removal are shown. As shown in Table 2, the higher R^2 value proves that TNT degradation follows the pseudo-first-order kinetic model. Considering the reaction rate constants, the efficacy of the investigated processes is as follows: PS/PF/O_3 > PF/O_3.

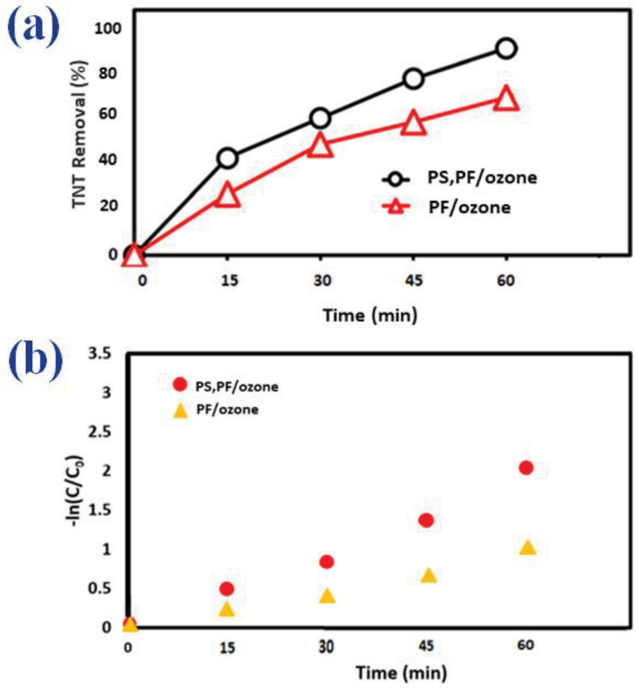

Fig. 8. Optimum reaction condition in two integrated processes: (a) TNT removal and (b) kinetic reaction (pH = neutral, oxidant = 19 mM (persulfate/potassium ferrate), TNT = 40 mg/L as optimum condition).

In order to better highlight the investigated processes, the synergistic effect of the reaction was calculated based on the following equations at 60 min reaction time [20]:

$$\text{Synergistic effect of PF on PS / O}_3 = \left[K_{\text{PS/PF/O}_3}\left(K_{\text{PS/O}_3} + K_{\text{PF}}\right)\right] \tag{17}$$

$$\text{Synergistic effect of PF on O}_3 = \left[K_{\text{PF/O}_3}\left(K_{\text{PF}}\right)\right] \tag{18}$$

Calculating the synergistic effects showed that PF addition to the PS/O_3 leads to the highest synergistic effect of 8.4, and then PF/O_3 process contributed to 7.9 synergistic effects on the TNT removal efficiency. Therefore, the combination of the two investigated processes makes the PS/PF/O_3 process an efficient and reliable technique for TNT degradation.

3.6. Bioassay test

As expected, stock solution was most toxic, with EC_{50} values of 1,026 µg/mL (24 h), 1,013 µg/mL (48 h), 998 µg/mL (72 h) and 971 µg/mL (96 h). Analysis of the related results displayed a considerable treatment effect due to the concentration of organism exposure at each time.

The treated red-water bioassay test on *D. magna* showed the underneath ranking: stock solution (most toxic) >> PF/O_3 effluent > PS/PF/O_3 (least toxic).

This phenomenon can be described that no harmful or toxic product is generated during the PF oxidizing process, and the final by-product ferric ion is an excellent energy source that can help grow up *D. magna* [43]. Meanwhile, these results confirm LC–MS analysis. Consequently, it is important to notice that this system can oxidize 2,4,6-trinitrotoluene to non-toxic compounds.

4. Conclusion

The present study investigated potassium ferrate as an integrated green excellent activator for the PS/O_3 AOP-based process (PS, PF/O_3).

The highest removal efficiency was achieved at a neutral pH value and oxidant dose of 19 mM. Undermentioned conditions, 40 mg/L of TNT was degraded within 60 min responding to the almost 89.3% of chemical oxygen demand removal, 75.7% of total organic carbon removal by PS/PF/O_3 process; and 77.2% chemical oxygen demand removal, 82.1% of the total organic carbon removal by PF/O_3, respectively. In PS/PF/O_3 process, PF presented a preferable factor for the simultaneous activation of the PS/O_3 process. In the mentioned condition, 2,4,6-trinitrobenzaldehyde, 2,4,6-trinitrobenzoic acid, and 1,3,5-trinitrobenzene were the main intermediates detected by LC–MS analysis. Also, this reaction chain was subsequently continued, and nitrate ions were identified as a key factor for mineralization. Degradation of TNT was in accordance with the pseudo-first-order kinetic model ($R^2 = 0.98$).

Bioassay test also demonstrated a considerable reduction in toxicity after each process, and the dispersion test of *D. magna* assay on treated red-water ranked as follows: stock solution (high toxicity) >> PF/O_3 effluent > PS/PF/O_3 (low toxicity). It can be concluded that the combination of the two investigated processes makes the PS/PF/O_3 process an efficient and reliable technique for TNT degradation.

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