ORIGINAL PAPER

Optimization and evaluation of the efficiency of sono-Fenton and photo-Fenton processes in the removal of 2, 4, 6 trinitrotoluene (TNT) from aqueous solutions

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ABSTRACT

The adverse health effects of trinitrotoluene (TNT) include allergies, liver and blood damage, and carcinogenesis. The present study aimed to optimize the sono-Fenton and photo-Fenton processes for the removal of TNT from aqueous solutions. TNT removal was evaluated at various pH (acidic, neutral, and alkaline), pollutant concentrations (10, 30, 50, 100, and 120 mg/L), H_2O_2 concentration (10-80 mM), and ferrous ions (0.5-4 Mm). After the optimization of the parameters, the appropriate UV irradiation time and optimal time of ultrasonic waves were determined for the removal of this compound. TNT concentration was measured using high-performance liquid chromatography. Increased hydrogen peroxide from 10 to 40 mMole/L led to higher TNT degradation (45.3 to 88.4% and 40 to 80 mMole/L), while the removal rate decreased from 88.4 to 79%. At the optimal H_2O_2 concentration, increased pH (3±0.2 to 11±0.2) decreased TNT decomposition from 88.4 to 23.5%. In addition, increased time (5 to 60 minutes) led to the higher photo-Fenton process efficiency (68.6 to 89%). The maximum photo-Fenton efficiency was achieved in optimal conditions at the TNT concentration of 10 mg/L (97%) and 60 minutes, while the efficiency of the sono-Fenton process in optimal conditions was 100% at 20 minutes. Therefore, it was concluded that the sono-Fenton process was effective in the removal of TNT.

Keywords: Hydroxyl Radical, Trinitrotoluene, Water Resources, Ultrasonic Waves, UV Radiation

Introduction

Over the past decades, the production of 2, 4, 6 trinitrotoluene (TNT) and other explosives in munitions factories has increased the concentration of these pollutants in soil and water. The US Environmental Protection Agency (EPA) has classified TNT as a hazardous substance in terms of carcinogenicity, categorizing it as a priority pollutant (Group C). Moreover, the USEPA has recommended the dose of 0.2 mg/L per day per a 10-kilogram infant as a standard level for drinking water.[1-3] Some of the adverse health effects of TNT include allergies, liver damage, weakened immune system, skin irritation, loss of appetite, anemia, and carcinogenicity.[1]

Several methods are used for the removal of organic compounds (especially explosives). Advanced oxidation processes (AOPs) is a common approach in this regard.[4-8] Among various types of AOPs, the Fenton process has shown significant potential for the

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decomposition of harmful organic compounds.[9,10] This process is based on the production of hydroxyl radicals (OH•) as a result of the reaction between H_2O_2 and ferrous ions (Fe^{2+}) in acidic conditions.[11-13] The Fenton process in combination with UV light leads to the production of hydroxyl radicals through the optical regeneration of ferric ions (trivalent) into bivalent iron, as well as the photocatalysis of hydrogen peroxide. In the sono-Fonton process, ultrasonic waves and sono-chemistry (sonolysis) produce bubbles through cavitation. Cavitation involves the formation, growth, and explosion of the produced bubbles in aquatic environments by ultrasonic waves, thereby resulting in the production of radical hydroxyl.[14-17]

According to the study by Oh *et al.* regarding the removal of TNT and RDX from aqueous solutions using the Fe/H_2O_2 process, if iron zero-valent is used as pre-treatment, the iron treatment and oxidation of Fenton leads to the oxidation of more than 95% of these compounds.[18] In another research, Hoffmann e*t al.* used the sono-chemical method to remove chemical pollutants from water and sewage solutions. According to the findings, the removal rate largely depended on the ultrasonic frequency.[19]

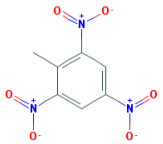
In a similar study, Amin *et al.* used an advanced oxidation method based on ozone and hydrogen peroxide in order to remove TNT from aqueous solutions, and the obtained results demonstrated that the maximum decomposition efficiency of TNT (90% removal) was achieved at the pH of 3, initial TNT concentration of 10 mg/L, and hydrogen peroxide-to-TNT ratio of 1000:1.[20] Another study by Chen and Huang regarding the removal of dinitrotoluene and trinitrotoluene from sewage was conducted using a combination of titanium dioxide nanoparticles ultrasonic (sono-chemical), and the results indicated that the ultrasonic waves increased the rate of nitrotoluenes removal.[21]

To date, the comparison of sono- and photo-Fenton for TNT removal has not been investigated in Iran. On the other hand, the synergistic effects of ultrasonic and Fenton processes on TNT removal is considered to be a novel approach. The present study aimed to optimize the sono-Fenton and photo-Fenton processes by changing the influential factors in the removal of trinitrotoluene from the aqueous phase.

Materials and Methods

In the present study, TNT was provided by the local munitions manufacturing plants. The other chemicals used in the research were obtained from Sigma-Aldrich (USA). Table 1 shows the physicochemical properties of TNT.[22]

Table 1. Physicochemical properties of TNT

Chemical formula	$C_7H_5N_3O_6$
Chemical structure	
Molecular weight	227.13
Melting point	80.1 °C
Boiling point	240 °C
Water solubility at 20 °C	130 mg/L
Vapor pressure	1.99×10^{-4} mm Hg
Henry's law constant (20 °C)	4.57×10^{-7} atm-m^3/mole

This study was conducted on a laboratory scale using a 200-mL reactor equipped with a UV lamp and an ultrasonic device. Fig. 1 shows the schematic of the reactor.

A synthetic solution was prepared by dissolving TNT in deionized water. To do so, 126.32 mg of TNT (95% purity) was added to deionized water and stirred at the temperature of 70 °C for four hours. Initially, the desired amount of TNT was mixed with methanol, and after dissolution, water was added to the desired volume. At the next stage, the rate of TNT removal at various pH (acidic, neutral, and alkaline) was investigated using the photo-Fenton process at the optimum pH, where maximum TNT removal was obtained. In order to adjust the pH, sulfuric acid and potassium hydroxide (0.1 M) were used.

At the following stage, the optimal pH obtained in the previous step was used to assess the TNT removal rate at five concentrations of the pollutant (10, 30, 50, 100, and 120 mg/L). Since the dissolution of TNT in water was approximately 0.57 mmol/L (130 mg/L) at the

temperature of 20 °C,[7] the maximum concentration of TNT was 0.53 mmol/L (120 mg/L). In the third step, the optimal dose of hydrogen peroxide (10-80 mmol/L) was determined in the photo-Fenton and sono-Fenton processes, and the molar ratio of Fe: H_2O_2 was optimized. After the optimization of the relevant parameters, the optimal irradiation time of UV light and ultrasonic waves was determined for the removal of the compound. After performing the reaction at each stage, TNT concentration was measured using high-performance liquid chromatography (HPLC).

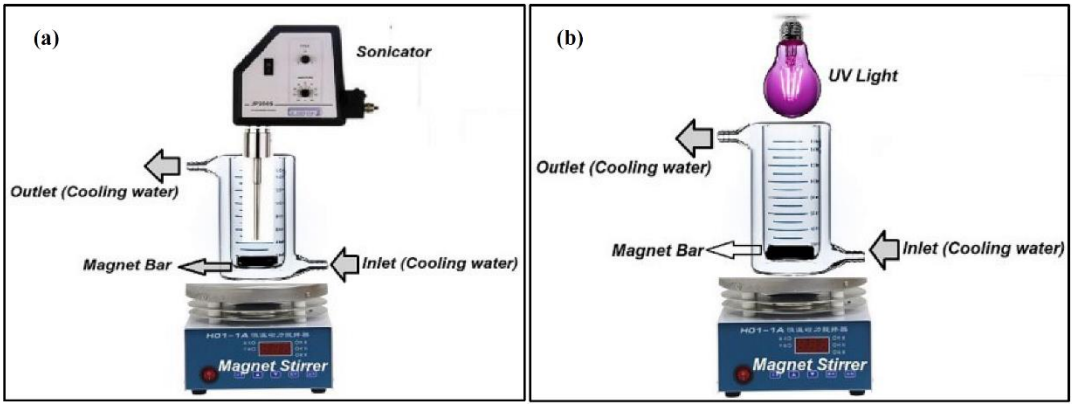


Fig. 1. Schematic of reactor: a) Sono-reactor, b) Photo-reactor

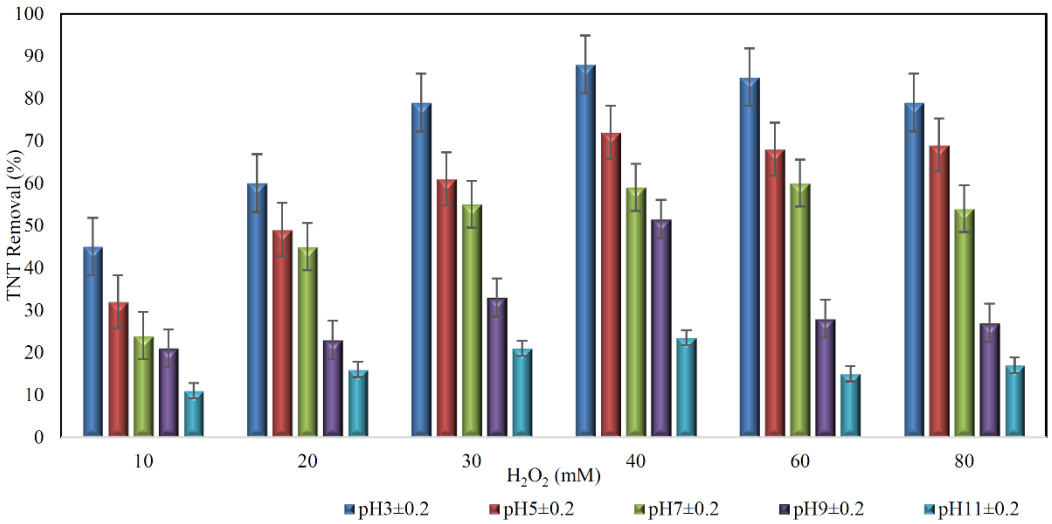


Fig. 2. Effects of hydrogen peroxide concentrations (various pH) on removal of TNT by photo-Fenton and sono-Fenton processes

All the experiments in the current research were carried out based on the standard methods for examination of water and wastewater,[23] and the obtained results were presented in graphs using the Excel software.

Results and Discussion

Effects of the concentration of hydrogen peroxide at various pH on the photo-Fenton and sono-Fenton processes for TNT removal

Fig. 2 depicts the effects of various levels of hydrogen peroxide (10-80 mmol/L) at different pH. Accordingly, in acidic conditions, increased hydrogen peroxide from 10 to 40 mM/L caused the TNT degradation rate to increase from 45.3 to 88.4% and from 40 to 80 mM/L, while the efficiency decreased from 88.4 to 79%.

In general, pH is an important parameter in the Fenton process, which affects the concentration of ferrous ions (Fe^{2+}) and radical hydroxyl production. According to our findings, the TNT decomposition rate decreased with

increased pH. At the optimum concentration of hydrogen peroxide, increased pH from 3±0.2 to 11±0.2 caused the decomposition rate to decrease from 4.44 to 23.5%.

Radical hydroxyl is considered to be a key factor in oxidation in the Fenton process. The reduction of TNT decomposition in the presence of excessive hydrogen peroxide is due to the effect of excessive hydrogen peroxide scavenging. Some hydroxyl radicals are consumed by Fe (II) (Eq.1) and H_2O_2 (Eq. 2), inhibiting the oxidative activity of radical hydroxyl. Reactions two and three respectively show the OH• reactions with H_2O_2 and Fe^{2+}.[24] Therefore, it could be inferred that up to the optimal levels of hydrogen peroxide (40 mM/L), the removal efficiency of TNT increased, while the process efficiency decreased in the presence of excess hydrogen peroxide. As a result, 40 mM of hydrogen peroxide was considered as the optimum concentration. Similar results have been reported in the other studies in this regard.[24, 25]

$$Fe^{2+} + OH\bullet \longrightarrow Fe^{3+} + OH^{-} \quad (1)$$

$$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \quad (2)$$

According to the results of the present study, the efficiency of the Fenton process improved in acidic conditions. At high pH levels, Fe^{3+} was involved in two competitive reactions, and two ferric complexes of $Fe\text{-}O_2H^{2+}$ and $Fe(OH)_3$ were formed (Eqs. 3 and 4).

$$Fe^{3+} + H_2O_2 \longrightarrow Fe{-}O_2H^{2+} + H^{+} \quad (3)$$

$$Fe^{3+} + 3OH^{-} \longrightarrow Fe(OH)_3 \quad (4)$$

In the Sono- Fenton process, ultrasonic reacts with the $Fe\text{-}O_2H^{2+}$ complex and based on Eq. 5, Fe^{2+} are formed

$$Fe{-}O_2H^{2+} \xrightarrow{))))} Fe^{2+} + HO_2\bullet \quad (5)$$

According to the findings, the $Fe(OH)_3$ complex was stable. Through the formation of this complex, the reduction of Fe^{2+} was weakened. Therefore, the maximum degradation efficiency of TNT was obtained at lower pH levels. Similar behaviors have been reported in the previous studies in this regard.[26-30] At high pH levels, excess hydrogen peroxide decomposes without participation in the oxidation reaction. In addition, increased pH causes ferrous ions to be converted into ferric ion, thereby reacting with hydroxyl radicals and producing ferric hydroxide, while reducing the availability of the ferrous ions in the solution.[31]

Fig. 3 shows the results of exposure to UV radiation at various pH levels. Accordingly, increased time from five to 60 minutes increase the photo-Fenton process efficiency from 68.6 to 89%, while after 40 minutes (optimal pH conditions), the removal efficiency of TNT did not increase significantly (from 40 to 60 minutes, the efficiency increased only 1%). As a result, 40 minutes was selected as the optimal time, which is consistent with the results obtained by Matta *et al*.[32]

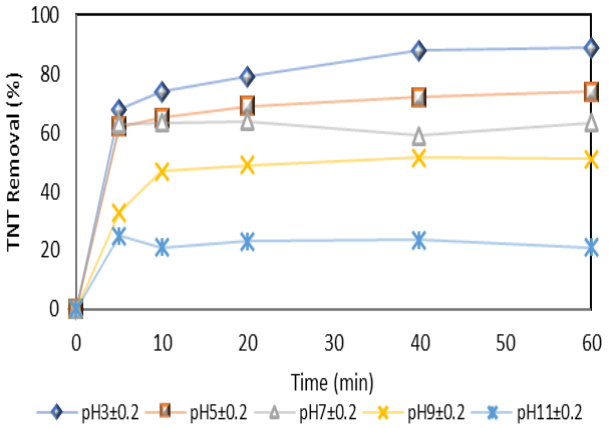


Fig. 3. Effect of UV radiation time at different pH levels on TNT removal

Effect of UV radiation time in the photo-Fenton process on TNT removal

Fig. 3 depicts the results of UV radiation exposure at various pH levels. With the increased time from five to 60 minutes, the photo-Fenton process efficiency increased from 68.6 to 89%. After 40 minutes (optimal pH conditions), the removal efficiency of TNT did not increase significantly (from 40 to 60 minutes, the efficiency increased only 1%).

Effect of Fe^{2+} concentration

According to the findings of the current research, the increased concentration of ferrous ions led to the increase rate of TNT removal. As is depicted in Fig. 4 (in 40 minutes, pH of 3 and 40 mmol/L of hydrogen peroxide), the increased concentration of the ferrous ions from 0.5 to 4 mM caused the TNT degradation rate to increase

from 88.4 to 95.2%. Therefore, at the concentration of 2 mM, the process efficiency was 93%, and increased Fe^{2+} (up to 4 mM) was only associated with 2% removal. Therefore, the concentration of 2 mM was considered optimal for ferrous ion.

According to the findings of the current research, the produced radical hydroxyl increased with higher Fe^{2+}. Ferrous ions are a catalyst in the Fenton reaction, which increase the production of radical hydroxyl. The results of the present study indicated that the addition of Fe(II) to constant amounts of hydrogen peroxide (Eq. 6) led to higher hydroxyl radicals.[24] Fe^{2+} is a catalyst in the Fenton process, and as the catalyst increases, radical hydroxyl production increases as well.[27]

$$Fe^{2+} + H^{+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + H_2O \quad pH=3 \quad (6)$$

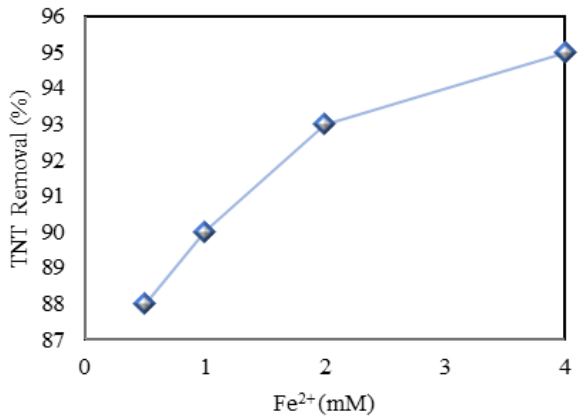


Fig. 4. Effect of Fe^{2+} concentration in Fenton process on TNT removal

Effect of TNT concentration

According to our findings, increased TNT concentration was associated with the decreased efficiency of the photo-Fenton and sono-Fenton processes. As is shown in Fig. 5, at 60 minutes, increased TNT concentration from 10 to 120 mg/L resulted in the reduced process efficiency from 97.7 to 72.3%.

The obtained results of the present study demonstrated that increased TNT concentration was associated with the lower photo-Fenton and sono-Fenton process efficiency. Since the rate of hydroxyl radical formation in the specified conditions (pH of 3, 2 mM of ferrous ions, and 40 mM of hydrogen peroxide) was constant, increased TNT concentration led to the reduced removal efficiency of this compound.

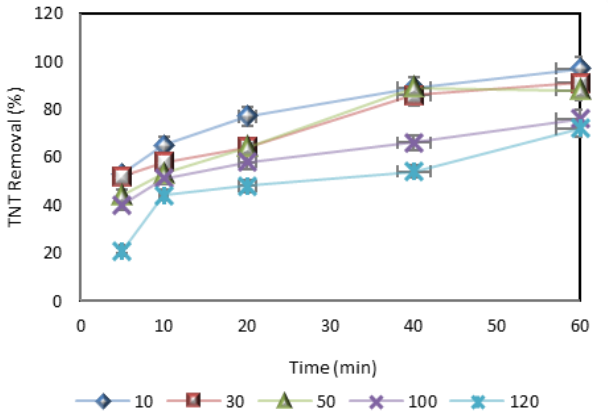


Fig. 5. Efficiency of photo-Fenton process (different concentrations of TNT) in TNT removal at various UV radiation times

Effect of ultrasonic time and power in the sono-Fenton process on the removal of TNT

Fig. 6 shows the effects of ultrasonic waves on the removal efficiency of TNT. It is notable that this section of the Results is presented in terms of α ($\alpha = \frac{TNT_{out}}{TNT_{in}}$). As is depicted Fig. 6-a, in the optimal conditions obtained from Fig. 6-b (ultrasonic optimum power=400 W) with the increased ultrasonic time, the efficiency of the sono-Fenton decomposition process increased.

According to our findings, increased ultrasonic power was associated with the higher TNT degradation. As the ultrasonic power increased, the number of the collapsing bubbles also increased. In addition, increased radical hydroxyl production was associated with the higher ultrasonic power.[27] On the other hand, Fig. 6-a shows that in the optimal conditions obtained from Fig. 6-b (ultrasonic power=400 W), the increased ultrasonic time enhanced the efficiency of decomposition in the sono-Fenton process.

According to our findings, increased ultrasonic power was associated with the higher TNT degradation. As the ultrasonic power increased, the number of the collapsing bubbles also increased. In addition, increased radical hydroxyl production was associated with the higher ultrasonic power.[27] On the other hand, Fig. 6-a shows that in the optimal conditions

obtained from Fig. 6-b (ultrasonic power=400 W), the increased ultrasonic time enhanced the efficiency of decomposition in the sono-Fenton process.

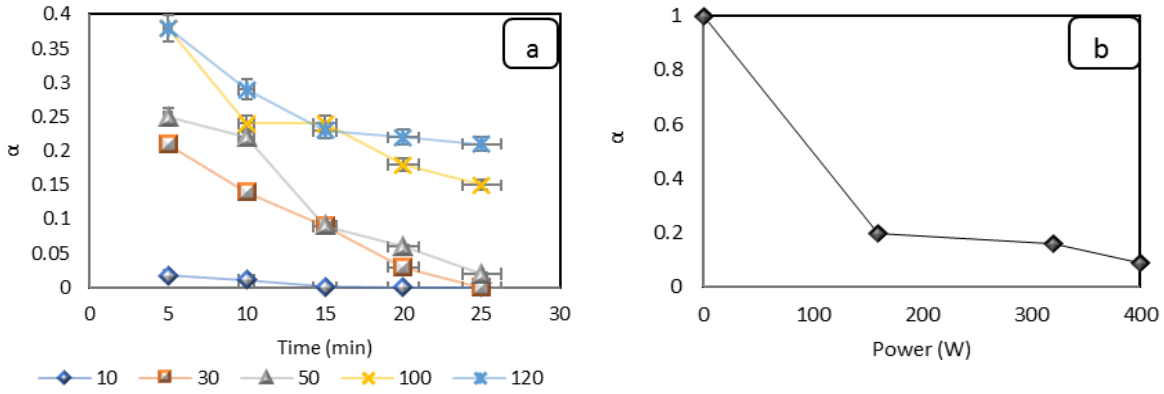


Fig. 6. a) Effect of ultrasonic time (optimal power=400 W) on TNT removal in sono-Fenton process; b) Effect of ultrasonic power on TNT removal in sono-Fenton process

During the reaction between ferric ions (Fe^{3+}) and hydrogen peroxide, the Fe-OOH^{2+} complex was produced. The reduction of Fe^{2+} from this complex by the ultrasonic waves was observed to increase the concentration of Fe^{2+} in the solution (Eq. 5). On the other hand, Eq. 7 shows that water sonolysis also produced hydroxyl radicals, so that the TNT decomposition would increase in the sono-Fenton process.[27]

$$H_2O \overset{))))}{\longrightarrow} OH\bullet + {}^{\circ}H \quad (7)$$

The synergistic effects of ultrasonic and Fenton

To compare the effects of the ultrasonic waves in the Sono-Fenton process and Fenton and ultrasonic alone, the synergistic index (SI) was calculated using Eq. 8, as follows:

$$SI = \frac{Eff_{US/Fe^{2+}+H_2O_2}}{Eff_{US}+Eff_{Fe^{2+}+H_2O_2}} \quad (8)$$

where Eff_{US}, $Eff_{Fe^{2+}+H_2O_2}$, and $Eff_{US/Fe^{2+}+H_2O_2}$ represent the decomposition rate by the ultrasonic waves, Fenton, and photo-Fenton processes, respectively. The SI of the reaction was estimated at 1.28, which indicated the significant effects of the ultrasonic waves on the sono-Fenton process. Therefore, the efficiency of the sono-Fenton process was higher compared to the ultrasonic waves and Fenton alone.

Reaction kinetics

The kinetic equations, their parameters, and amount are presented in Table 2.

Table 2. Relevant parameters of kinetics for TNT removal

Kinetics	Non-Linear	Linear	Parameter	Value
Pseudo-first reaction	$q = q_e(1 - e^{-tk_1})$	$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}$	$q_{e(cal)}$ mg/g k_1 R_2	0.335 3.28 0.8978
Pseudo - second-order reaction	$q = \frac{K_2 q_e^2 t}{1 + K_2 q_e^2 t}$	$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$	$q_{e(cal)}$ mg/g k_2 h R_2	7.81 0.0048 0.2941 0.9932

In Fig. 7, K_1 is the pseudo-first-order constant, K_2 is the constant pseudo-second reaction rate, q_t shows the TNT value at time t (mg/g), and q_e is the constant of the pseudo-second-order reaction (g/mg/min). The results of the present study indicated that the kinetics of the TNT removal reaction followed the pseudo-second-order equation (r^2=0.96).

In the investigation of the photo-Fenton and sono-Fonton processes, the results of the r^2

coefficient indicated that the TNT decomposition reaction followed the pseudo-second-order reaction (Fig. 8). Our findings are consistent with the study by Amin *et al.* regarding the elimination of TNT by ozonation and hydrogen peroxide.[20]

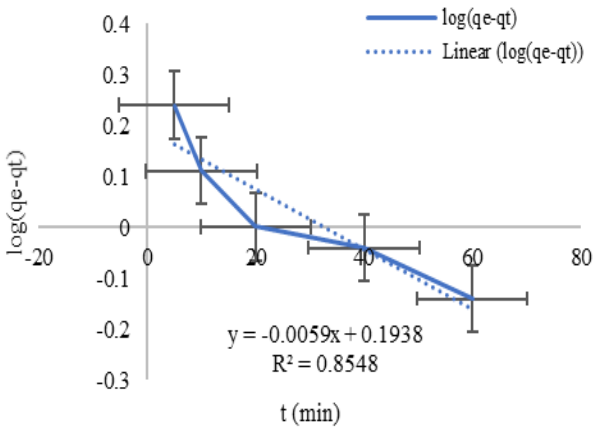


Fig. 7. First-order kinetics for removal of TNT in sono-Fenton process

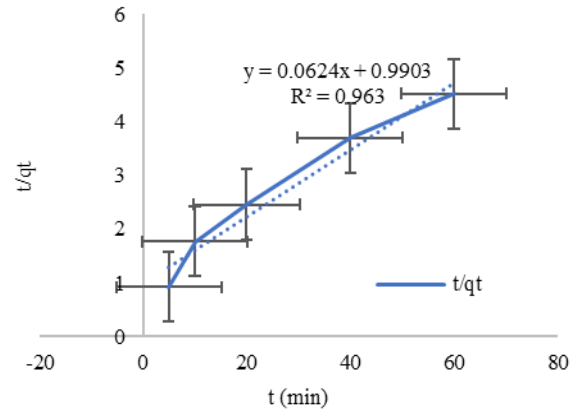


Fig. 8. Pseudo-second-order kinetics for removal of TNT in sono-Fenton process

Conclusion

We investigated the efficiency of the sono-Fenton and photo-Fenton processes in the removal of TNT from aqueous solutions. According to the results, increased Fe(II) at constant amounts of hydrogen peroxide led to higher radical hydroxyl production, which improved the process efficiency. In addition, the maximum photo-Fenton efficiency was obtained in the optimal conditions at the TNT concentration of 10 mg/L (97%) and 60 minutes, while the efficiency of the sono-Fenton process in the optimum conditions was 100% at 20 minutes. Therefore, it could be concluded that the sono-Fenton process was more effective in TNT removal, and the SI results also showed that the efficiency of the sono-Fenton process was higher compared to the ultrasonic waves and Fenton alone.

Acknowledgements

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