

2,4,6-Trinitrophenol (2,4,6-TNP) degradation in aqueous solutions by Photo-Fenton and Photo-Fenton like systems

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ABSTRACT

The chemical degradation of 2,4,6-TNP in water by photo-Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$) and photo-Fenton like ($\text{H}_2\text{O}_2/\text{Fe}^{3+}/\text{UV}$) processes was investigated. A laboratory set-up was designed to evaluate and select the optimal oxidation process. The degradation rate is strongly dependent on the pH, temperature, H_2O_2 , iron (Fe^{2+} and Fe^{3+}), and $[\text{H}_2\text{O}_2]_0/[\text{iron}]_0$ ratio. The effect of these parameters has been studied and the optimum operational conditions of these two processes were found. The optimum conditions were obtained at pH 3, $\text{H}_2\text{O}_2 = 1.7 \text{ mmol}^{-1}$, iron = 0.0093 mmol^{-1} for the $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ and $\text{H}_2\text{O}_2/\text{Fe}^{3+}/\text{UV}$. The kinetics of degradation was found to followed first-order reaction rules. The photo-Fenton like system proved to be the most efficient and occurs at a much higher oxidation rate than photo-Fenton system and allows achieving 100% degradation of 2,4,6-TNP in 90 min of reaction time. The results of the study showed that photo-Fenton like process was an effective and economic treatment process for 2,4,6-TNP under acidic conditions by producing higher mineralization efficiency in a relatively short radiation time compared to other AOPs.

Keywords - 2,4,6-Trinitrophenol; Advanced oxidation processes (AOPs); photo-Fenton; photo-Fenton.

I. INTRODUCTION

Conventional wastewater treatment technologies have limitations hence demanding advanced research to tackle complex wastewater treatment. One of the promising technologies could be the use

of single chemical oxidants, or the more effective destruction by the use of advanced oxidation processes (AOPs) [1].

Industrial use of phenol and its derivatives over the past decades has led to severe environmental pollution. These pollutants have high toxicity and carcinogenic character. They have caused considerably damage to the ecosystem and human health. They are notified as potential toxic compounds by United States Environmental Protection Agency (USEPA) and their maximum allowable concentrations in water ranged from 1 to 20 ppb [2]. The total waste generation comprising these hazardous substances in the southern state of Andhra Pradesh, India is estimated as 6884 t per month (TPM). Out of this around 190.3 TPM constitute phenolic wastes disposed mainly by petrochemicals, pharmaceuticals and polymer industries [3]. Photooxidative degradation plays an important role in the degradation of these pollutants into the components that are nontoxic and safe for human health. In other words, photooxidative degradation is a system, which operates at room temperature and being used for the purification of polluted water and decomposition of toxic organic pollutants. These processes are based on the generation of the highly reactive hydroxyl radical capable of unselectively react with most of organic and inorganic substances present in drinking water and wastewaters. Homogenous advanced oxidation process employing hydrogen peroxide with UV light has been found to be very effective in the degradation of organic compounds [4–6]. This process involves the production of hydroxyl radicals ($\cdot\text{OH}$) that are extremely reactive and strong

oxidizing agent ($E^0 = 2.8$ V) capable of mineralizing organic contaminants. Reaction of hydroxyl radicals generated in the presence of an organic substrate may occur via one of the three general pathways: (1) hydrogen abstraction; (2) electrophilic addition; (3) electron transfer [7]. The AOPs process in comparison to other methods of water treatment has additional advantages such as no formation of sludge during the treatment and high removal rates of chemical oxygen demand (COD) [8].

It is now common to use Fe^{2+} and H_2O_2 to generate hydroxyl radicals [9,10] for oxidizing organics:



Recently, it was shown that a treatment process using Fe^{3+} and H_2O_2 with the aid of UV radiation (photo-Fenton like process) is an effective alternative for the degradation of organic pollutants present in the soil or ground water [11,12]. It facilitates the photolysis of aquated Fe^{3+} ions to give $\cdot\text{OH}$ and regenerate Fe^{2+} for Fenton's reaction (Eq. (1)):



Where $\text{Fe}(\text{OH})^{2+}$ refers to $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$.

This electron transfers process has been efficiently used to study the degradation of several organic pollutants in aqueous solution [13,14]. Mazellier and Bolte [15,16] used this process for the degradation of 4- and 3-chlorophenol in aqueous solution. However, this reaction is pH and wavelength dependent [11,17] at which the quantum yield of $\cdot\text{OH}$ and ferrous ion formation decreased at longer wavelengths.

The main objective of this study is to analyse the feasibility of degradation of 2,4,6-TNP by photo-Fenton and photo-Fenton like processes. The influence of different operational parameters (pH, temperature, H_2O_2 , Fe^{2+} , Fe^{3+} and 2,4,6-TNP concentration) which affect the efficiency of photo-Fenton and photo-Fenton like reactions, in 2,4,6-TNP oxidation was also investigated.

1. Experimental

1.1. Reagents

All chemicals were used as received, in which 2,4,6-TNP, iron (II) sulphate-7-hydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and iron (III) sulphate-1-hydrate ($\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$) were purchased from Merck. All stock solutions were prepared in previously boiled and cold, double distilled water and 2,4,6-TNP was prepared at 0.3 mmol l^{-1} and directly used for reaction study. FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ were freshly made in distilled water and dilute sulphuric acid is added to prevent the hydrolysis. Hydrogen peroxide (30% w/w) was purchased from Merck.

1.2. Photoreactor

All experiments were carried out in a 1.0 liter jacketed thermostatic glass photoreactor (diameter 81 mm and height 320 mm,) equipped with low pressure mercury lamp (8 W, UV-C, manufacture by Philips, Holland) which emitted a maximum radiation at 252.4 nm was placed in its center axially. The outside of the reactor was covered with an aluminium sheet. At the top, the reactor has inlets for feeding reactants, and ports for measuring the temperature and withdrawing samples. The reactor is equipped with a magnetic stirrer used a Teflon coated magnetic bar for homonisation of solution at the constant rate of 600 rpm achieved by using dimmerstat. All the reactions were performed at atmospheric pressure. The temperature was maintained at 30 ± 0.2 °C or adjusted at different temperature if required by circulating the water from a cryostat bath (Fourtech systems, Mumbai, India).

1.1. Experimental procedure and analytical methods

All the experiments were carried out in batch mode. In each experiment a 2,4,6-TNP solution of 68.73 mg l^{-1} (0.3 mmol l^{-1}) was prepared with double distilled water by using stock solution of $3436.65 \text{ mg l}^{-1}$ (0.015 M). The solutions were perfectly mixed to guarantee that all 2,4,6-TNP was dissolved, and the required pH of solution was adjusted initially by using dilute 0.01 N H_2SO_4 or

NaOH when required. Every time the photoreactor was charged with 800 ml solution, the required concentrations of iron salt Fe^{2+} or Fe^{3+} were added when necessary. A 30% aqueous H_2O_2 solution was injected into the reactor at different concentrations and the UV-light was switched on at the same time. During the experiments, samples were withdrawn from the reactor at several time intervals.

The change in 2,4,6-TNP concentration was measured with UV-visible double beam spectrophotometer (Spectrascan UV 2600, Chemito, India) at 357 nm, the quartz cuvette of 1 cm of path length was used while recording the spectra. A calibration plot based on Lambert's law was established by relating the absorbance to the concentration. COD measurements were conducted in accordance with the titrimetric open reflux method [18].

Total organic carbon (TOC) was measured by direct injection of the filtered samples into a Shimadzu-5000A, TOC analyser calibrated with standard solution of hydrogen potassium phthalate.

2. Results and discussion

In the photo-Fenton and photo-Fenton like processes, the H_2O_2 was decomposes and $\cdot\text{OH}$ was produced. The formation and quantity of $\cdot\text{OH}$ depends on several factors such as pH, temperature, dose of Fe^{2+} , Fe^{3+} and H_2O_2 , initial concentration of the pollutant and the ratio between Fe^{2+} , Fe^{3+} and H_2O_2 . Therefore, the effects of the previous factors were investigated.

3.1. Chemical degradability of 2,4,6-TNP To evaluate the efficiency and the benefit of each condition on the 2,4,6-TNP degradation experiments were carried out under the following conditions: (1) 2,4,6-TNP+ H_2O_2 , (2) 2,4,6-TNP+UV (3) 2,4,6-TNP+ H_2O_2 +UV, (4) 2,4,6-TNP+UV+ H_2O_2 + TiO_2 , (5) 2,4,6-TNP+UV+ H_2O_2 + Fe^{2+} (photo-Fenton process), (6) 2,4,6-TNP+UV+ H_2O_2 + Fe^{3+} (photo-Fenton process like) in Fig. 1 are represented the results of degradation. From the results it is possible to observe that 2,4,6-TNP is resistant to the oxidation from H_2O_2 alone. As expected, the direct photolysis

(UV alone) is not an efficient process in this experiment and can be neglected since less than 3% of conversion within 90 min of UV illumination occurred. The combined action of UV and H_2O_2 caused 67% degradation in 90 min. For UV, H_2O_2 and TiO_2 2,4,6-TNP removal observed was 69% in 90 min. In photo-Fenton process 2,4,6-TNP removal was 99.5% at 90 min. For photo-Fenton like process 100% of degradation was obtained at 90 min. Therefore, photo-Fenton and photo-Fenton like processes are more efficient than other experimental conditions. The relative efficiencies of the above processes are in the following order: $\text{Fe}^{3+}+\text{H}_2\text{O}_2+\text{UV}$ (photo-Fentonlike) $>$ $\text{Fe}^{2+}+\text{H}_2\text{O}_2+\text{UV}$ (photoFenton) $>$ $\text{TiO}_2+\text{H}_2\text{O}_2+\text{UV}$ $>$ $\text{UV}+\text{H}_2\text{O}_2$ $>$ UV $>$ H_2O_2 . The high efficiency of photo-Fenton and photo-Fenton like process is due to the formation of more hydroxyl radical than the other processes. In combination of thermal process and UV light

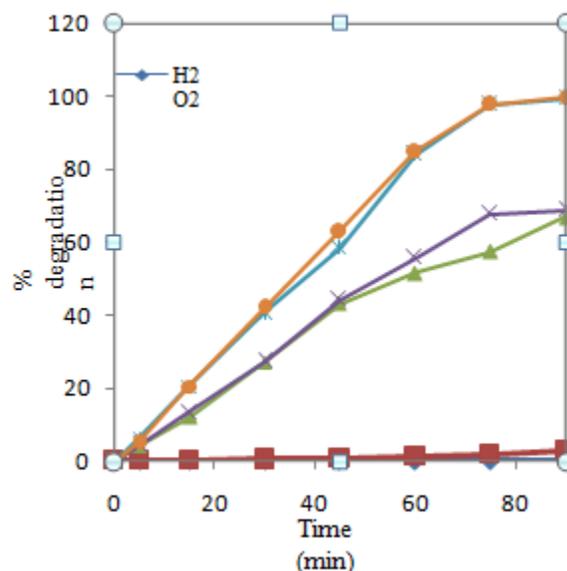
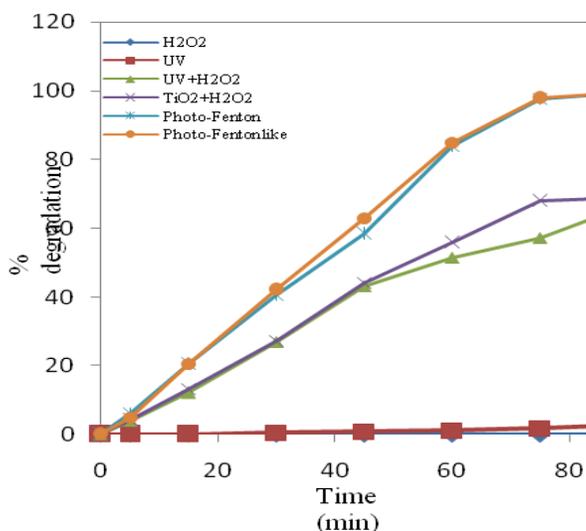


Fig. 1. Chemical degradability of 2,4,6-TNP under different conditions. Initial conditions: pH 3, Temp. $^{\circ}\text{C} = 30 \pm 0.2$, $[\text{2,4,6-TNP}]_0 = 0.3 \text{ mmol l}^{-1}$, $[\text{Fe}^{2+}]_0 = [\text{Fe}^{3+}]_0 = 9.3 \times 10^{-3} \text{ mmol l}^{-1}$ and $[\text{H}_2\text{O}_2] = 1.7 \text{ mmol l}^{-1}$.



the oxidation power of Fenton reagent was significantly increased due mainly to the photo-reduction of Fe^{3+} to Fe^{2+} , which could react with H_2O_2 establishing a cycle mechanism of generating additional hydroxyl radicals (Eq. (4)). Furthermore, the effect of UV light was also attributed to the direct hydroxyl radical formation and regeneration of Fe^{2+} from the photolysis of the complex $\text{Fe}(\text{OH})^{2+}$ in solution. It was known that the existing form of ferrous iron was connected with the acidity of solution. At about pH 3, a part of ferrous iron would exist as the form of $\text{Fe}(\text{OH})^{2+}$, whose photolysis under UV illumination could directly produce $\cdot\text{OH}$ radical and Fe^{2+} , as indicated below (Eq. (3)).



Therefore, higher degradation rate and percentage of 2,4,6-TNP came out in the photo-Fenton and photo-Fenton like system.

3.2. Degradation kinetics

The disappearance of 2,4,6-TNP during the first 90 min of oxidation could be described as a pseudo first-order reaction kinetics with regard to 2,4,6-TNP concentration as it may be seen from the data in Fig. 2. Degradation rate constants, k (in min^{-1}), were determined from the slope of $-\ln(C_t/C_0) = t$ (min) plots, where C_0 and C are the concentration of 2,4,6-TNP at times 0 and t .

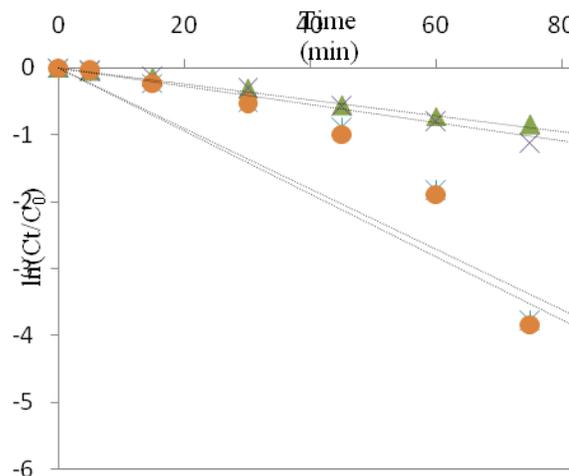


Fig. 2. First-order plot for degradation of 2,4,6-TNP by different systems. Conditions were similar as Fig. 1.

The apparent rate constant has been chosen as the basic kinetic parameter to compare the different systems, since it is independent on the concentration and, therefore, enables one to determine the catalytic activity. Also, to have a better knowledge on the degradation process is presented the time necessary to reduce to 50% the initial concentration of 2,4,6-TNP the half life time ($t_{1/2}$). The results are listed in Table 1.

The experimental data in Fig. 2 show that photo-Fenton like processes had a significant accelerating effect on the rate of oxidation of 2,4,6-TNP. The data in Table 1 show that adding Fe^{3+} to the $\text{UV}+\text{H}_2\text{O}_2$ system enhanced the rate of 2,4,6-TNP oxidation by a maximum factor 4.17 and 4.09 while Fe^{2+} addition, over the $\text{UV}+\text{H}_2\text{O}_2$ system, depending on both H_2O_2 and Fe doses. This phenomenon of enhanced efficiency is also known from other investigations with Fe^{2+} and Fe^{3+} [19]. As listed in Table 1, the addition of TiO_2 to the $\text{UV}+\text{H}_2\text{O}_2$ system show little acceleration in rate constant for 2,4,6-TNP degradation (from 0.011 to 0.013 min^{-1}). However, the studied photo-Fenton and photo-Fenton like processes shows higher rate constant and degradation capacity of 2,4,6-TNP. This is because UV light in presence of H_2O_2 can

Table 1
First-order rate kinetics (k) and half-life ($t_{1/2}$) of 2,4,6-TNP degradation.

Type of oxidation process	k (min^{-1})	$t_{1/2}$ (min)
UV+H ₂ O ₂	0.011	63.01
UV+H ₂ O ₂ +TiO ₂	0.013	53.32
UV+H ₂ O ₂ +Fe ²⁺	0.045	15.40
UV+H ₂ O ₂ + Fe ³⁺	0.047	14.75

significantly influence direct formation of $\cdot\text{OH}$ radicals as well as the photo-reduction rate of Fe³⁺ to Fe²⁺ (Eq. (4)). So, to have a complete knowledge of optimal conditions for each process, the next steps of this work are to assess the capacity of each process (photo-Fenton and photo-Fenton like), to oxidize 2,4,6-TNP, evaluating the effect of each parameter fixing the values of the others.

3.3. Effect of pH

The pH value affects the oxidation of organic substances both directly and indirectly. The photo-Fenton and photo-Fenton like processes are strongly pH dependent. The pH value influences the generation of hydroxyl radicals and thus the oxidation efficiency. The effect of pH on the degradation of 2,4,6-TNP by photo-Fenton and photo-Fenton like processes is shown in Fig. 3.

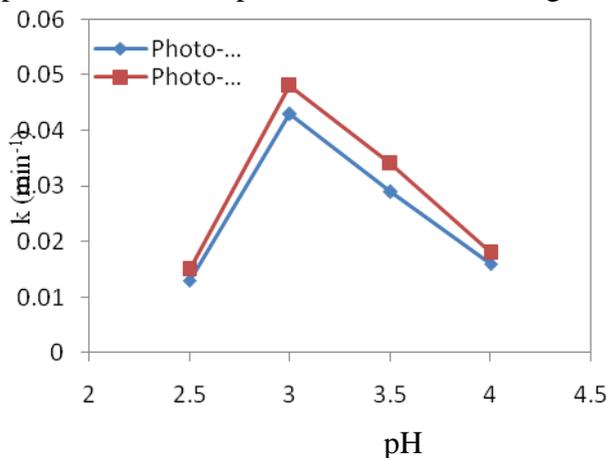


Fig. 3. Rate constant (k min^{-1}) vs. pH for the degradation of 2,4,6-TNP at different initial pH in photo-Fenton and photo-Fenton like processes. Temp. $^{\circ}\text{C} = 30 \pm 0.2$, $[2,4,6\text{-TNP}]_0 = 0.3$ mmol^{-1} , $[\text{Fe}^{2+}] = [\text{Fe}^{3+}] = 0.93 \times 10^{-2}$ mmol^{-1} and $[\text{H}_2\text{O}_2]_0 = 1.7$ mmol^{-1} .

This figure shows that pH significantly influences the degradation of 2,4,6-TNP. The experiments were carried out at pH with in the range 2.5–4. In all this range, the degradation by photo-Fenton like is higher than photo-Fenton process. At low pH (<3) we have a less degradation both in photo-Fenton and photo-Fenton like process. By increasing the pH to 3 we can obtain the highest rate constant for both the systems. These results are in agreement with those reported in previous studies [20,21]. The optimum pH was found to be about 3. The degradation decreased at pH values higher than 3.2, because iron precipitated as hydroxide, which resulted in a reduction in the transmission of the radiation (photo-Fenton) [22]. Additionally, the oxidation potential of hydroxyl radical was known to decrease with increasing pH [23]. Another reason for the inefficient degradation at pH > 3 is due to the dissociation and auto-decomposition of H₂O₂ [24]. For pH values below 3, the reaction of hydrogen peroxide with Fe²⁺ is seriously affected causing the reduction in hydroxyl radical production. The low degradation at pH < 3 is also due to the hydroxyl radical scavenging of H⁺ ions (Eq. (5)) [23]



3.4. Effect of H₂O₂ dosage

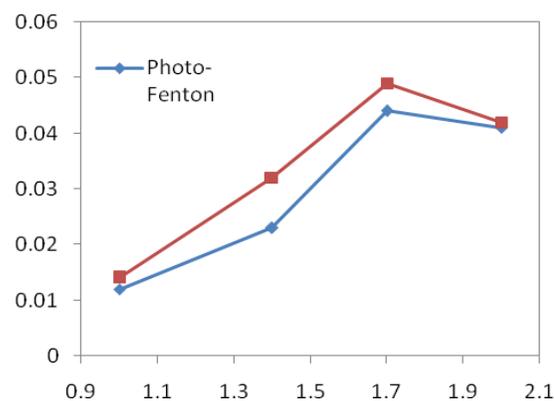
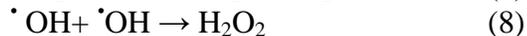
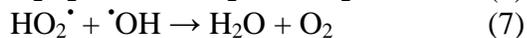
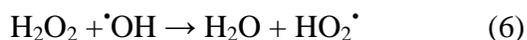


Fig. 4. Rate constant ($k \text{ min}^{-1}$) vs. $[\text{H}_2\text{O}_2]_0$ for the degradation of 2,4,6-TNP at different initial H_2O_2 in photo-Fenton and photo-Fenton like processes. pH 3, Temp. $^{\circ}\text{C} = 30 \pm 0.2$, $[\text{2,4,6-TNP}]_0 = 0.3 \text{ mmol l}^{-1}$, and $[\text{Fe}^{2+}] = [\text{Fe}^{3+}] = 0.93 \times 10^{-2} \text{ mmol l}^{-1}$.

Fig. 4 shows the relationship between rate constant for the degradation of 2,4,6-TNP and initial concentration of H_2O_2 for photo-Fenton and photo-Fenton like processes. To render the photo-Fenton and photo-Fenton like processes competitive with other processes, it is essential that their applications represent a low cost operation, which basically implies a better control of H_2O_2 dosage. The objective of this evaluation is to select the best operational dosage of H_2O_2 in photo-Fenton and photo-Fenton like processes. In these experiments, the original concentration of H_2O_2 was changed from 1.0 to 2.0 mmol l^{-1} , but the concentration of Fe^{2+} and Fe^{3+} was kept constant. The results indicate that the degradation of 2,4,6-TNP was increased by increasing the concentration of H_2O_2 . This can be explained by the effect of the additionally produced hydroxyl radicals. With increasing H_2O_2 concentration from 1.0 to 1.7 mmol l^{-1} for photo-Fenton and photo-Fenton like processes, the rate constant increases but above this range the improvement was not obvious. This may be due to recombination of hydroxyl radicals and also hydroxyl radicals reaction with H_2O_2 , contributing to the $\cdot\text{OH}$ scavenging capacity (Eqs. (6)–(8)) [19].



It can be postulated that H_2O_2 should be added at an optimum concentration to achieve the best degradation. Hence, 1.7 mmol l^{-1} of H_2O_2 appears as an optimal dosage for photo-Fenton and photo-Fenton like processes.

3.5. Effect of ferrous and ferric dosage

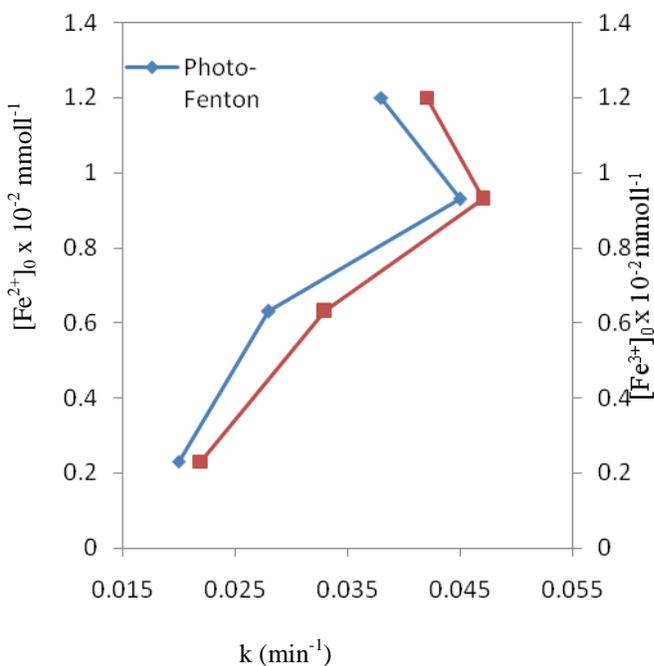


Fig. 5. Rate constants ($k \text{ min}^{-1}$) vs. dosage of Fe^{2+} and Fe^{3+} for the degradation of 2,4,6-TNP at different initial concentration of Fe^{2+} and Fe^{3+} in photo-Fenton and photo-Fenton like processes. pH 3, Temp. $^{\circ}\text{C} = 30 \pm 0.2$, $[\text{2,4,6-TNP}]_0 = 0.3 \text{ mmol l}^{-1}$ and $[\text{H}_2\text{O}_2]_0 = 1.7 \text{ mmol l}^{-1}$.

Addition of iron salt, ferrous or ferric is one of the main parameters to influence the photo-Fenton and photo-Fenton like processes respectively. In this study, to obtain the optimal initial Fe^{2+} and Fe^{3+} concentration, the investigation was carried out in the range of (0.0023–0.012 mmol l^{-1}) at pH 3 and $[\text{H}_2\text{O}_2]_0 = 1.7 \text{ mmol l}^{-1}$. The results for photo-Fenton and photo-Fenton like processes are shown in Fig. 5.

It can be seen that the degradation rate of 2,4,6-TNP distinctly increased with the increasing amount of iron. So, for the photo-Fenton process, the addition of Fe^{2+} from 0.0023 to 0.0093 mmol l^{-1} increases the rate constant of reaction from 0.020 to 0.045 min^{-1} and in the photo-Fenton like process the increase is from 0.022 to 0.047 min^{-1} . The rate constant of 2,4,6-TNP began to decrease when the concentration of both Fe^{2+} and Fe^{3+} was higher than 0.0093 mmol l^{-1} . It is known that iron has a catalytic decomposition effect on H_2O_2 . When the iron concentration increased, the catalytic effect also accordingly increased. When the concentration of

Fe^{2+} was higher, a great amount of Fe^{3+} from the process of H_2O_2 decomposition by Fe^{2+} was easy to exit in the form of $\text{Fe}(\text{OH})^{2+}$ in acidic environment. Because $\text{Fe}(\text{OH})^{2+}$ had a strong absorption for UV light from 290 to 400 nm, the strength of UV light would decrease [25]. Therefore, the decrease in the degradation rate of 2,4,6-TNP would occur. Iron of $0.0093 \text{ mmol l}^{-1}$ can be used as an optimum dosage for both the processes.

3.6. Effect of the temperature

Degradation of 2,4,6-TNP was carried out at five different temperatures (from 293 to 313K)

As it can be expected the temperature exerts a strong effect on 2,4,6-TNP degradation rate, which is increased at high temperature due to an increment in the first-order rate constant.

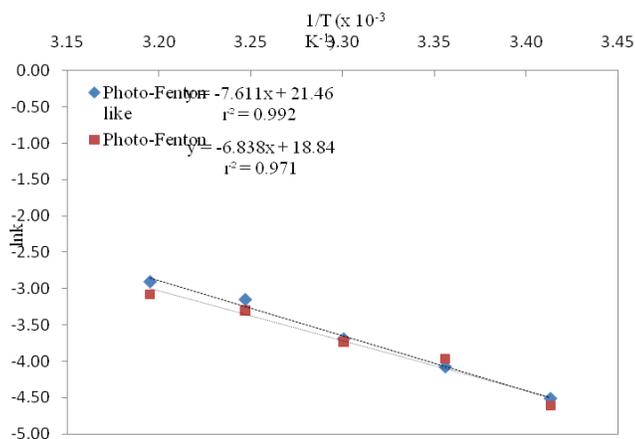


Fig. 6. Plot of $\ln k$ vs. $1/T$ for the degradation of 2,4,6-TNP.

pH 3, $[2,4,6\text{-TNP}]_0 = 0.3 \text{ mmol l}^{-1}$ $[\text{Fe}^{2+}$ and $\text{Fe}^{3+}]_0 = 0.0093 \text{ mmol l}^{-1}$ and $[\text{H}_2\text{O}_2]_0 = 1.7 \text{ mmol l}^{-1}$.

The data exhibiting an Arrhenius type behavior with an activation energy of 56.85 and 63.28 kJ mol^{-1} was calculated for photo-Fenton and photo-Fenton like process from the usual $\ln(k)$ vs $1/T$ (Fig.6)

It is interesting to note that the activation energy is calculated for photo-Fenton like process higher than that measured for photo-Fenton process.

3.7. Mineralisation study

In order to assess the degree of mineralisation reached during AOPs, the decrease of the total

organic carbon (TOC) is estimated. To investigate the mineralisation degree of 2,4,6-TNP in Fenton and photo-Fenton processes, the experiments of 2,4,6-TNP degradation were conducted at 2,4,6-TNP initial concentration of 0.3 mmol l^{-1} . The amount of TOC produced by the degradation reaction was measured. Productivity of TOC was regarded as mineralisation efficiency. The results are shown in Table 2.

As could be seen, 2,4,6-TNP degradation is much higher than TOC removal even in photo-Fenton and photo-Fenton like. Although, it is visible from this table that photo-Fenton like process presents a TOC removal higher than photo-Fenton process, 43.97% and 42.12%, respectively. The great difference between degradation efficiency and mineralisation efficiency also implied that the products of 2,4,6-TNP oxidation mostly stayed at intermediate products stage under the present experimental conditions.

Table 2

Comparison between the degradation and TOC removal of 2,4,6-TNP by photo-Fenton and photo-Fenton like

Oxidation processes	Degradation (%)	TOC (%)
Photo-Fenton	99.5	42.12
Photo-Fenton like	100	43.97

Experimental conditions: pH 3, Temp. $^{\circ}\text{C} = 30 \pm 0.2$, Reaction time = 90 min, $[2,4,6\text{-TNP}]_0 = 0.3 \text{ mmol l}^{-1}$, $[\text{Fe}^{2+}]_0 = 0.5 \text{ mmol l}^{-1}$, and $[\text{H}_2\text{O}_2]_0 = 1.7 \text{ mmol l}^{-1}$.

3. Conclusions

The results showed that photo-Fenton and photo-Fenton like processes are powerful methods for degradation of 2,4,6-TNP, but photo-Fenton like process is more efficient. The degradation rate and percentage were influenced by the pH of solution, temperature, the amount of hydrogen peroxide and iron salt. 2,4,6-TNP degradation follows, even for

photo-Fenton and photo-Fenton like, a pseudo first-order kinetic law. The optimum conditions for the degradation of 2,4,6-TNP in photo-Fenton and photo-Fenton like processes were observed at pH 3, with an initial iron concentration of $0.0093 \text{ mmol l}^{-1}$ and initial H_2O_2 concentration of 1.7 mmol l^{-1} with a 2,4,6-TNP concentration of 0.3 mmol l^{-1} . Photo-Fenton like was more efficient than photo-Fenton, not only for 2,4,6-TNP degradation but also for TOC mineralisation. The advantages of both these processes as an oxidative treatment are low cost, rapid degradation, and simple handling. Therefore, both systems would be applied to wastewater treatment works as a new developing methodology for reducing levels of other pesticides, especially in countries with abundant solar light.

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