

Employing UV/H₂O₂ Process for Degradation of 2,4-Diaminotoluene in Synthetic Wastewater

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Background & Aims of the Study: Toluene-2, 4-diamine (TDA) is a famous carcinogenic aromatic amine that is mostly employed as an intermediate in the production of dyes and toluene diisocyanate. In this study, degradation and mineralization of TDA were investigated by UV/H₂O₂ process.

Materials & Methods: This study is an experimental investigation on a laboratory scale. The study was performed on synthetic wastewater that holds TDA. The influence of different operating variables such as the initial dosage of H₂O₂ and TDA, additive salts and pH was investigated. The optimization of variables was done by one factor at a time method.

Results: The results specify that the degradation efficiency relies on the H₂O₂ and TDA concentrations, so that, reduces as the initial concentrations of TDA are improved, but, it enhances with increasing the extent of H₂O₂ until an optimum value and then decreases to some extent. The reaction rate significantly reduced with an increase in initial pH value in alkaline solution, which means hydroxide ions could inhibit the degradation of TDA. The removal time was increased with an increase in the initial concentration of TDA. The optimal conditions were obtained at pH of 7, initial concentration of pollutant and hydrogen peroxide at 0.5×10^{-3} M and 3.5×10^{-2} M, respectively. At optimum condition, the removal of TDA and Chemical Oxygen Demand (COD) was 97.6 and 43.5%, respectively.

Conclusions: The results of this work show that separate UV radiation and H₂O₂ oxidation process can hardly degrade TDA from contaminated water and the UV/H₂O₂ process can be employed for complete degradation of TDA. The removal of TDA in UV/H₂O₂ process follows the pseudo-first order kinetics and the first order rate constants ($k = 35.7 \times 10^{-3} \text{min}^{-1}$) and half-life of reaction ($t_{1/2} = 19.4 \text{min}$) were determined.

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Background

2,4-Toluene diamine (TDA) is a main carcinogenic raw material for the manufacture of toluene diisocyanate (TDI), dye corrosion inhibitors, rubber antioxidants and polyurethane foams (1). They can be transferred to surface water through wastewater discharge from industrial plants. TDA has high water solubility and it can penetrate through soil causing the groundwater contamination

(2–3). Aromatic amines are environmental pollutants that are mutagenic in microorganisms and mammalian cells which have been reported to be cancer-causing in rodents.

Despite the wide range of the conventional methods such as biological and physical-chemical treatment (coagulation–flocculation, and activated carbon adsorption), they are not suitably efficient because dyes are scarcely removable according to their low molecular

weight and high water solubility. Furthermore, the conventional methods are not destructive but only extract the pollution from one phase to another, thus a secondary pollution is handled and extra treatments are considered essential (4–6). Several advanced oxidation processes (AOPs) have been suggested and widely used for the degradation of many toxic, non-biodegradable, carcinogenic and mutagenic contaminants (7).

The AOPs based on the UV/H₂O₂ system had high efficiency in the degradation of several Organic pollutants (8). The UV/H₂O₂ process has many benefits such as high removal of COD and no production of sludge (9). Usually, the oxidation products are low molecular weight of oxygenated compounds that are biodegradable or reduce to water and carbon dioxide. The radiation should be used to photolyse the H₂O₂ molecules with a wavelength, lower than 400 nm. In the UV/H₂O₂ process the photolysis of hydrogen peroxide produces effective oxidizing species, hydroxyl radicals (OH•) with a quantum yield of two hydroxyl radicals formed per quantum of radiation absorbed (10), according to the following reaction:



The oxidation potential of hydroxyl radical is 2.8 eV, which can completely destroy the pollutants existing in the wastewater or change them to simple harmless intermediates.

Aims of the study: In this study the synthetic wastewater containing TDA was selected and the main purpose is to inspect the degradation and mineralization of TDA by UV/H₂O₂ process. The effect of different operational variables such as the initial concentration of H₂O₂ and TDA, additive salts and pH was investigated.

Materials & Methods

Materials

TDA (98%) was purchased from Sigma-Aldrich, China. The stock solution of TDA was synthesized with distilled water. The hydrogen

peroxide solution (30%), NaOH and H₂SO₄ were obtained from Merck, Germany. All chemicals were of reagent grade and employed without further purification.

Table 1) Chemical structure and maximum wavelength of TDA.

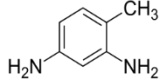
| Pollutant | Molecular structure | λ_{max} , nm | M_w (g mol ⁻¹) |
|----------------------------|---|----------------------|------------------------------|
| Toluene-2, 4-diamine (TDA) |  | 230 | 122 |

Photo reactor:

All experiments were performed in a batch photo reactor. The radiation source was a low pressure mercury UV lamp emitting at 254 nm (15W, UV-C, manufactured by Philips, Holland) which was positioned above the reactor horizontally (11). The intensity of light was measured by a Lux-UV-IR meter from Leybold Company. The light intensity was changed by varying the distance between the lamp and the surface of the solution and it was fixed at 35Wm⁻² in all of this research. In each experiment, 1000 ml of TDA solution with definite amounts of hydrogen peroxide was conveyed to the reactor. Then the UV lamp was switched on to start the reaction and the solution was mixed with a constant rate by magnetic stirrer. About, 2ml of the sample was taken out at certain reaction intervals and the concentration of TDA was determined.

Analytical Procedure

The concentration of TDA was measured by spectrophotometric method and then validated by High-performance liquid chromatography (HPLC) equipped with an ultraviolet detector at 224 nm and a reverse phase column, filled with 3 μm Separon C₁₈ which was 150 mm in length and 4.6 mm in diameter. The isocratic method with a solvent mixture of Acetonitrile–phosphate buffer (20 mM, pH=7.0, 30/70, v/v)

was used as the mobile phase at the flow rate of 1.0 mL min⁻¹ and the column temperature was set at 30°C. The retention time for TDA was 4.69 min.

Samples were withdrawn and then analyzed by a UV-Vis spectrophotometer (Agilent, 5453, American) at 230 nm. The Calibration plot based on the Beer Lambert's law was used by concerning the absorbance to the concentration. The decrease in the absorbance at 230 nm is due to the degradation of TDA. The COD was determined as described in the previous work (12). The efficiencies were estimated with respect to its initial value and the removal percent for the TDA and COD was obtained as (Eqs. 2-3):

$$\text{Removal of TDA}(\%) = \left(\frac{(TDA)_0 - (TDA)}{(TDA)_0} \right) \times 100 \quad (2)$$

$$\text{Removal of COD}(\%) = \left(\frac{(COD)_0 - (COD)}{(COD)_0} \right) \times 100 \quad (3)$$

Where (TDA)₀ and (COD)₀ are the concentration of the TDA and amount of COD at the start of the reaction; (TDA) and (COD) are the concentration of TDA and amount of COD at time t, respectively.

Results

Effect of the initial concentration of H₂O₂

The experimental data exhibited that the UV and H₂O₂ process have a slight effect on the degradation of TDA when they were used separately (data not showed here). Many researchers have stated that the concentration of H₂O₂ has a main effect on the UV/H₂O₂ process (8,13). The degradation efficiency of TDA versus irradiation time at different initial dosages of H₂O₂ has been shown in Fig.1. It was increased from 61.3 to 84.5% by increasing the concentration of H₂O₂ from 2 × 10⁻² to 3.5 × 10⁻² M at pH of 9.

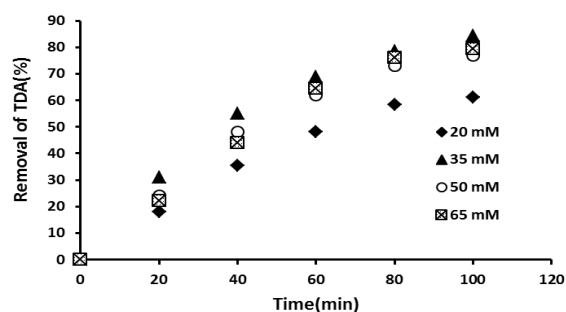


Figure 1) Effect of initial dosage of hydrogen peroxide in degradation of TDA ([TDA]₀ = 0.5 × 10⁻³ M, time=100 min and pH= 9).

Influence of initial pH of the solution

The pH value has a significant effect in the UV/H₂O₂ process. The influence of initial pH of 4, 7 and 9 was investigated from 2 × 10⁻² to 3.5 × 10⁻² M of H₂O₂ (Fig. 2). The results were displayed that the degradation of TDA depends on pH. When the initial pH of the solution was enhanced from 4 to 7, the removal of TDA was enhanced from 76 to 97.6% in 100 min of reaction. The best pH was 7.

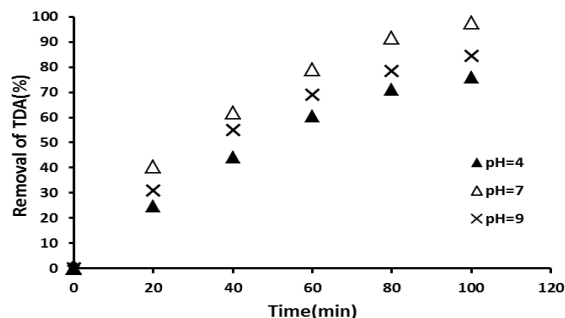


Figure 2) Effect of initial pH in degradation of TDA ([TDA]₀ = 0.5 × 10⁻³ M, [H₂O₂]₀ = 3.5 × 10⁻² M, and time=100 min).

Effect of the initial concentration of TDA

As it can be seen from Fig. 3, the concentration of TDA was changed from 0.5 to 1 mM to check its effect on the degradation efficiency. The removal efficiency at 100 min of reaction was decreased from 97.6 to 48%, with an increase in the initial concentration of TDA from 0.5 to 1 mM.

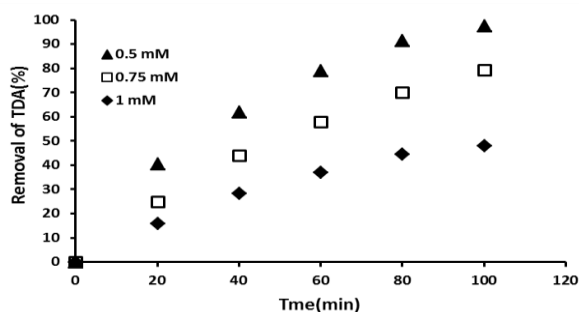


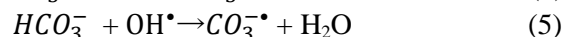
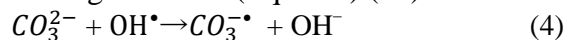
Figure 3) Effect of initial concentration of TDA in photo oxidative degradation of TDA ($[TDA]_0 = 0.5 \times 10^{-3}$ M, $[H_2O_2]_0 = 3.5 \times 10^{-2}$ M, and time=100 min).

Mineralization of TDA by UV/H₂O₂ process

The COD reduction was investigated to study the mineralization of TDA in UV/H₂O₂ process. The total concentration of organics in the solution has been presented by COD values. About 43.5% of COD was reduced at an initial concentration of TDA at 0.5 mM in the existence of 3.5×10^{-2} M of H₂O₂, at 100 min of irradiation. The intermediates produced by UV/H₂O₂ process were resistant to degradation. Consequently, the removal percent of COD was lower than the removal of TDA.

Influence of different salts on degradation of TDA

The addition of chemical salts such as NaCl, NaHCO₃ and Na₂CO₃ (0.8 g l^{-1}) on the photo oxidation of TDA was shown in Fig. 4. Among used salts, Na₂CO₃ and NaHCO₃ delay the removal rate and only 56 and 76.2 % of degradation was happened, respectively; in optimum conditions after 100 min of reaction. This inhibition is certainly due to their ability to act as hydroxyl radical scavengers by the following reactions (Eqs.4–5) (13):



The addition of NaCl does not affect the removal rate extensively. The small decrease in the removal efficiency (83.5%) is according to the hydroxyl radical scavenging effect of chloride ion by the following reactions (Eqs.6–7) (8):

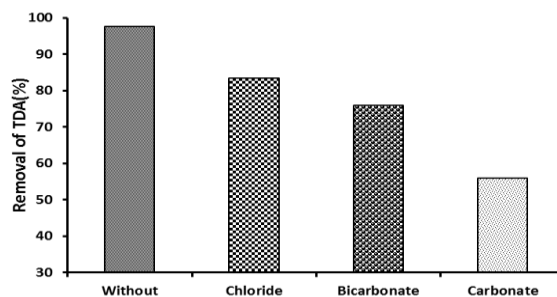
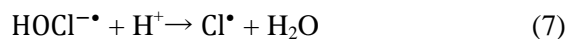


Figure 4) Effects of NaCl, NaHCO₃ and Na₂CO₃ on the degradation of TDA in UV/H₂O₂ process ($[TDA]_0 = 0.5 \times 10^{-3}$ M, $[H_2O_2]_0 = 3.5 \times 10^{-2}$ M, pH 7, $[Salts]_0 = 0.8 \text{ g l}^{-1}$ and time=100 min).

Effect of solution temperature

According to the experimental results, it is clear that the photo oxidative degradation is not affected by slight changes in temperature (14). In our experiments, the temperatures have been selected to simulate the operating condition at room temperature from 288 to 303 K. The effect of different initial water temperatures on the degradation has been investigated and the results are shown in Fig. 5.

As it can be seen from Fig. 6, the removal rate increases from 92.5% to 97.6 % by enhance in water temperature from 288 to 303 K at the time of 100 min. It is clear that the results point to the slight effect of the temperature on the degradation of TDA.

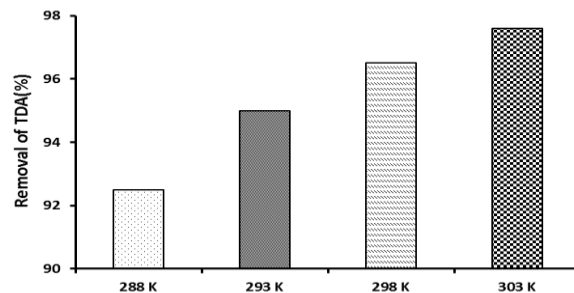


Figure 5) Effect of temperature on the degradation of TDA ($[TDA]_0 = 0.5 \times 10^{-3}$ M, $[H_2O_2]_0 = 3.5 \times 10^{-2}$ M, and time=100 min).

Kinetic study

According to the experimental results, it was clear that in optimum conditions, the numbers of hydroxyl radicals were 70 times higher than TDA, so hydroxyl radicals can be supposed to

be nearly fixed, hence the kinetic constant of reaction was achieved by fitting the experimental data, using Pseudo first order kinetic equations. This tactic was in agreement with previous studies [7,15].

As it can be seen from Fig.6, for appraising these rate constants, the term $\ln \frac{[TDA]_0}{[TDA]}$ versus reaction time was plotted, and after linear regression analysis, the first order rate constants ($k = 35.7 \times 10^{-3} \text{ min}^{-1}$) and half-life of reaction ($t_{1/2} = 19.4 \text{ min}$) were determined.

$$\ln\left(\frac{[TDA]_0}{[TDA]}\right) = k_{app} \times t \quad (8)$$

Where $[TDA]_0$ and $[TDA]_t$ are the concentration of TDA at times 0 and t, k_{app} is a pseudo-first-order rate constant and t is the time in min.

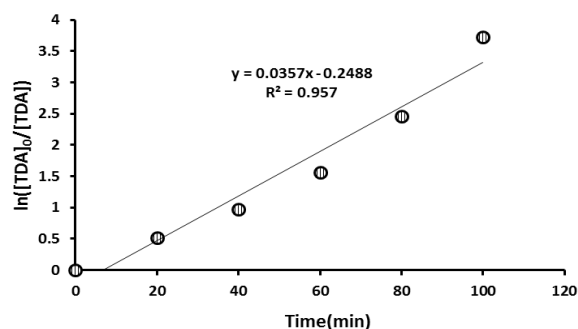
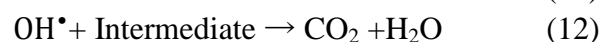
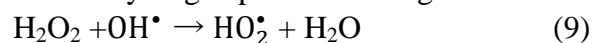


Figure 6) The curve of $\ln \frac{[TDA]_0}{[TDA]_t}$ versus reaction time in UV/H₂O₂ process (pH= 7, $[TDA]_0 = 0.5 \times 10^{-3} \text{ M}$, $[H_2O_2]_0 = 3.5 \times 10^{-2} \text{ M}$, and time=100 min).

Discussion

The improvement of degradation by adding of H₂O₂ is according to the enhancement in the hydroxyl radical concentration (Eq.1). At low concentration of H₂O₂, the removal rate is limited because enough hydroxyl radical cannot be generated. By increasing the initial concentration of H₂O₂ above $3.5 \times 10^{-2} \text{ M}$, the removal percent was decreased. The reason can be this phenomenon that when H₂O₂ employs in excess, hydroxyl radical reacts with H₂O₂ efficiently and creates hydro peroxy radical (Eq. (9)), that is weaker than hydroxyl radical.

In addition, the hydroxyl radicals originated at high concentration of H₂O₂ were dimerized to produce H₂O₂ (Eq. 10). So, in UV/H₂O₂ process, the removal of TDA is optimized at a critical hydrogen peroxide dosage.



The reaction rate considerably reduced with an increase in initial pH value in alkaline solution, which means hydroxide ions could inhibit the TDA degradation. The removal efficiency was decreased to 84.5% at pH of 9. This phenomenon is in agreement with the results of Guo (16). The hydrogen peroxide becomes unstable in alkaline pH and it is destroyed into water and oxygen (17), thus, H₂O₂ that is the source of OH[•] was reduced and the number of radicals was not enough to degrade TDA. Also, the pH decreased gradually during degradation of TDA because some intermediate products such as organic acids can be made during the process, causing the gradual decrease in the pH of the solution. The initial pH was 7 and dropped to 5.8 after 100 min of reaction.

The removal time with an increase in initial TDA concentration was improved. This can be described that both of the H₂O₂ and TDA absorb UV radiation in the range which was emitted by the lamp. A rise in the concentration of TDA causes an increase in the internal optical density and the solution exchanges more impermeable to UV radiation. At this condition, hydrogen peroxide can only be irradiated by a minor portion of UV light to produce lower free radicals. In addition, higher intermediates are formed at higher concentrations of TDA. These intermediates are highly resistant towards hydroxyl radicals. Thus, initial TDA and its intermediates compete proficiently for hydroxyl radicals, reducing the degradation efficiency (18).

Conclusion

The results showed that separate UV radiation and H₂O₂ oxidation process can hardly degrade TDA from contaminated water and the UV/H₂O₂ process can be employed for complete degradation of TDA. The results specify that the degradation efficiency relies on the pH, H₂O₂ and TDA concentrations, so, the reduction as the initial concentration of TDA is improved. The degradation efficiency enhances with increasing the extent of H₂O₂ until an optimum value and then decreases to some extent. The temperature has a minor effect on the degradation of TDA. The reaction rate considerably reduced with an increase in initial pH value in alkaline solution, which means hydroxide ions could inhibit the TDA degradation. The removal time with an increasing initial TDA concentration was enhanced. The removal of TDA in UV/H₂O₂ process follows the pseudo-first order kinetics and the first order rate constants ($k = 35.7 \times 10^{-3} \text{ min}^{-1}$) and half-life of reaction ($t_{1/2} = 19.4 \text{ min}$) were determined. After 100 min of reaction at optimum conditions, the removal of TDA and COD were 97.6 and 43.5%, respectively.

Footnotes

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Conflict of Interest:

The authors declared no conflict of interest.

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