

Influencing Factors and Kinetics of Degradation of Unsym-Dimethylhydrazine Waste Water by H₂O₂/UV/O₃ Process

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Keywords: Unsym-dimethylhydrazine (UDMH), ozone (O₃), Ultraviolet (UV), hydrogen peroxide

Abstract: The treatment of unsym-dimethylhydrazine (UDMH) waste water through H₂O₂ (hydrogen peroxide)/UV(ultraviolet) /O₃(ozone) combined process was carried out when temperature was 30.0±0.6°C and pH was 9.0±0.2. The influences of pre-treatment conditions, UV radiation intensity and wavelength ratio, O₃ dosing rate and initial concentration on the removal efficiency of UDMH and COD were researched. The results showed that the degradation rate of UDMH and COD increased as hydrogen peroxide dosage, aeration gas velocity and time of pre-treatment process, UV radiation intensity and O₃ dosing rate increased. And the rate decreased as the initial concentration increased, and the rate of ozone dosing and the intensity of ultraviolet radiation were the two factors that had the greatest impact on the reaction rate. The removal efficiencies of UDMH and COD were 100% and 98.62% at the UDMH concentration of 5000 mg·L⁻¹ for 60 min under the optimum conditions of the system. To conclude, there were significant synergistic effects in this system. In the initial stage, the reaction was mainly led by ultraviolet light while in the middle and late stages, the reaction was conducted and promoted by hydrogen peroxide.

1 INTRODUCTION

UDMH waste water is usually produced in the engine test, propellant transfer and rail tank cleaning process, which is characterized by intermittent generation, the composition, wide concentration range, high organic content (Xia et al., 2013). The main components of the waste water are UDMH, N-nitrosodimethylamine, nitromethane, 1,1,4,4-tetramethyl-2-tetrazene, organic nitriles, aldehydes, amines and so on (Liang et al., 2016). Most of which belong to the above-mentioned chemical toxic substances (GBZ/T 229.2; GBZ/T 230), and are carcinogenic, teratogenic and mutagenic. Its serious impact on the environment has attracted more people's attention (Angaji and Ghiaee, 2015).

Advanced oxidation processes (AOPs) are a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) materials in wastewater by oxidation through reactions with hydroxyl radicals ($\cdot\text{OH}$). According to the way of $\cdot\text{OH}$ generation and reaction conditions, it can be divided into photocatalysis, sonochemical oxidation,

ozonation, electrochemical oxidation and Fenton/Fenton-like methods.

These methods have been studied and applied in the field of UDMH waste water treatment in recent years. Jia Ying et al studied the photocatalytic degradation of UDMH waste water by ZnO/Pd. The experimental results showed that under natural light conditions, the degradation rate of UDMH reached 80.5% and the removal rate of COD reached 75.7 % (Jia et al., 2014). In the study on microwave-enhanced Fenton method conducted by Zhang Shujuan et al, the impact of different experimental conditions on the degradation efficiency of UDMH was studied. It was found that COD removal rate of UDMH waste water was up to 98.4% under the optimum conditions (Zhang et al., 2013). Jia Ying et al studied the degradation of UDMH wastewater through UV-Fenton method. In this study, they compared the degradation efficiencies of the five reaction systems designed. According to their results, COD removal rate of UDMH waste water could be up to 95.8% under the optimum conditions (Jia et al., 2009).

These oxidation processes have complex reaction systems and many refractory intermediates. Ozonating technology is getting more and more widely used in waste water treatment area, especially in difficult biodegradable pollutants treatment. This is because it has strong oxidizing properties and rapid reaction rates and no secondary-pollution will be produced (Lucas et al., 2010; Cao et al., 2016; Lee et al., 2016). However, due to the low diffusion rate of ozone in water and high operating costs, the application of it is subjected to many restrictions. In recent years, people have begun to study the combination of ozone and other methods to improve the utilization of O₃, such as UV/O₃, VUV/O₃, H₂O₂/O₃, H₂O₂/UV/O₃ and so on.

Based on the previous researches, the influence of different factors on the degradation rate of UDMH in H₂O₂/UV/O₃ system was analyzed in this paper, and the optimum conditions of the system were found out as well. The synergistic effect of this system was researched to study the degradation kinetics and provide a reference for the intermittent treatment of UDMH waste water.

2 EXPERIMENT

2.1 Experimental Device and Operating Conditions

H₂O₂/UV/O₃ combination process pilot test device is shown in Figure 1. The aeration tank with a capacity of 1.4m³ is made of 316L stainless steel. And it can be divided into three sections connected by flanges. The diameter of the upper section is 500 mm and the middle section is the reaction zone whose diameter is 900 mm. In the tank, six UV amalgam lamps (HANOVIA, 300W, radiation intensity:900μW·cm⁻²) are installed, in which four have the wavelength of 185 nm and two the wavelength of 254 nm. Each aeration tank has 12 aeration cylinders with a diameter of 150 mm. Exhaust pressure of the air compressor is 0.7 MPa. The volume flow and ozone generation rate are 6.7 m³·min⁻¹ and 20 Nm³·min⁻¹ separately. The gas purity is equal to or higher than 90%(vol). The ozone generated by ozone generator.

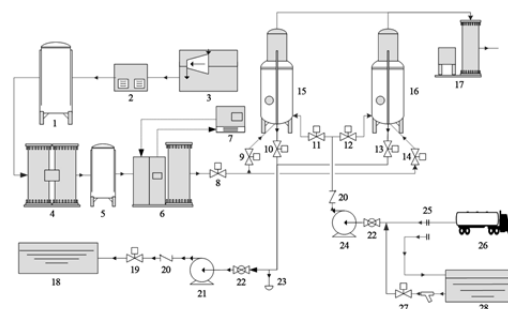


Figure 1: H₂O₂-UV-O₃ oxidation device and process.

1—gas holder; 2—air refrigeration dryer; 3—compressor; 4—oxygen generator; 5—buffer tank; 6—ozone generator; 7—chiller; 8,9,10,11,12,13,14,19,27—electrical valve; 15,16—reaction tank; 17—ozone destructor; 18—drainage basin; 20—check valve; 21—drainage pump; 22—manual valve; 23—sewage plug; 24—feed pump; 25—joints; 26—sewage lorry; 28—sewage reservoir (Qingdao Guolin, CF-G-2-2kg type) is 100~120 mg·L⁻¹ and the yield is 2 kg·h⁻¹.

2.2 Materials and Chemicals

GC-MS (Agilent 7890A-5975C); pH meter (Shanghai Leici, PHSJ-3F); UV light meter (Shenzhen Enci, UVX-254); HP8453E UV-Visible spectrophotometer (Agilent Technology); solid phase extraction column (Agilent Bond Elut-SCX).

UDMH (mass fraction was: UDMH, 99.59%; water, 0.03%; dimethylamine, 0.06%; formaldehyde dimethylhydrazone, 0.22%); hydrogen peroxide: 30% (analytical grade, Shanghai Taopu chemical plant); sodium hydroxide (analytical grade, Tianjin Beilian reagent plant); methanol (analytical grade, Tritical Company).

2.3 Experimental Process

The experimental process is shown below: (1) Pre-treatment process. The hydrogen peroxide solution (30% by mass) and saturated sodium hydroxide (analytical grade) was added into the UDMH sewage lorry or the sewage reservoir. The latter was 1% of the former by mass (GB 6920-86). After a certain period of air aeration, the pre-treatment process was completed. (2) Reaction process. The oxidation process was carried out in sequence of intermittent runs, in which about 2.0 m³ waste water was oxidized per cycle. After the pre-treatment,

UDMH waste water was added into aeration tank 1 by pump. Ozone was added after the generator ran steadily, then the UV lamp was turned on. After a certain time of reaction, it was switched to aeration tank 2 and the process was repeated the whole process was controlled by the programmable logic controller (PLC).

Unless changed in the paragraphs below, the reaction conditions were as follows: concentration of waste water $C_{\text{UDMH}}=5000 \text{ mg}\cdot\text{L}^{-1}$; reaction temperature $T=30.0 \text{ }^\circ\text{C}$, $\text{pH}=9.0$; pre-treatment gas velocity $V=1.5 \text{ m}^3\cdot\text{min}^{-1}$; pre-treatment time $t_{\text{pre}}=6 \text{ h}$; hydrogen peroxide dosage $D_{\text{hyp}}=47.2 \text{ g}\cdot\text{L}^{-1}$; UV radiation intensity $R=900 \text{ }\mu\text{W}\cdot\text{cm}^{-2}$; UV wavelength ratio 60% 185 nm + 40% 254 nm; ozone dosing rate $D_{\text{ozone}}=60 \text{ mg}\cdot(\text{L}\cdot\text{min})^{-1}$; reaction time $t_{\text{rea}}=60 \text{ min}$; UDMH removal efficiency and COD removal efficiency: ratio of experimental value to initial value (UDMH: $5000 \text{ mg}\cdot\text{L}^{-1}$, COD: $40000 \text{ mg}\cdot\text{L}^{-1}$).

2.4 Analytical Methods and Apparatus

PH was measured by pH meter (GB 6920-86) and H_2O_2 concentration by iodometric method (Gu and Li, 2004), and COD by potassium permanganate method (GB 11914-89), and radiation intensity by UV light meter.

Waste water was measured by GC-MS, Agilent 7693A Autosampler; Column: DB-1701 Capillary Column ($30 \text{ m}\times 0.25 \text{ mm}\times 0.25 \text{ }\mu\text{m}$). Analysis conditions: injection volume $1 \text{ }\mu\text{L}$; split injection; split ratio 1:40; carrier gas flow rate $1 \text{ mL}\cdot\text{min}^{-1}$; inlet temperature $200 \text{ }^\circ\text{C}$; programmed temperature: maintain at $50 \text{ }^\circ\text{C}$ for 5 minutes and rise to $160 \text{ }^\circ\text{C}$ at the rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and then maintain it for 3 minutes; EI ion source; mass scanning range: 29~280 amu; ion source temperature $230 \text{ }^\circ\text{C}$.

Waste water sample was pretreated by using solid phase extraction column. Extraction conditions: Solid phase extraction column was activated by 3 mL of methanol and balanced by 5 mL of deionized water. Then 4 mL of acidic sample (pH was about 3 to 4) was taken and the flow rate was no more than $1 \text{ mL}\cdot\text{min}^{-1}$. And then it was rinsed by 3 mL of methanol and 3 mL of deionized water and dried for 1 minute. Finally, it was eluted with 2 mL of saturated ammonia-methanol solution and collected.

3 RESULTS AND DISCUSSION

3.1 Influence of Pre-Treatment (Hydrogen Peroxide)

3.1.1 Influence of Hydrogen Peroxide Dosage

Taking the waste water of $C_{\text{UDMH}}=5000 \text{ mg}\cdot\text{L}^{-1}$ for example, the theoretical oxygen demand of UDMH mineralization in 1.0 L waste water was 1.17 mol, and the mass of hydrogen peroxide was 39.63 g. That is to say, the theoretical dosage D_{theory} was $132.08 \text{ g}\cdot\text{L}^{-1}$. When t_{pre} was 6 h, the relation between D_{hyp} and the removal efficiencies of UDMH and COD in waste water was shown in Figure 2.

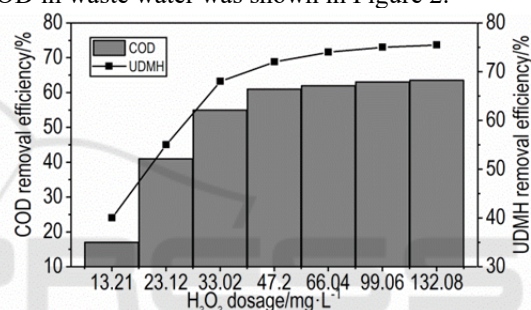


Figure 2: Influence of H₂O₂ dosage on removal efficiency of UDMH and COD.

As shown in the figure above, when D_{hyp} was $47.2 \text{ g}\cdot\text{L}^{-1}$, the removal efficiencies of UDMH and COD reached 76.5% and 63.4% separately. In the experiment, H_2O_2 was not added to fully mineralize UDMH and that left in solution was 54.3% of the dosage. The ratio of O_3 to H_2O_2 was between 1.4:1 and 0.9:1, and the ratio of H_2O_2 left to O_3 dosage could be maintained between 1.0:1 and 0.5:1 after the pre-treatment.

3.1.2 Influence of Aeration Gas Velocity and Pre-treatment Time

Air aeration not only helped to oxidize the solution but also stirred it during pre-treatment. The mass transfer of oxygen was a liquid membrane control process. The liquid mass transfer coefficient was improved as the gas velocity increased, thus improving the shock mixing effect. The influence of aeration gas velocity and pre-treatment time on UDMH removal efficiency when t_{pre} was 6 h~24 h was shown in Figure 3.

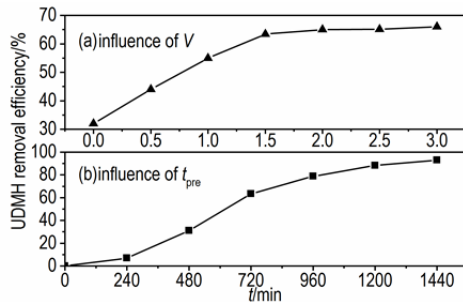


Figure 3: Influence of V and t_{pre} on removal efficiency of UDMH.

It can be seen from this figure that the removal efficiency of UDMH increased as V and t_{pre} increased, but the increase rate decreased due to the oxidation capacity limitation of H₂O₂. H₂O₂ was oxidized through a chain reaction. Subsequent products were easily generated during the pre-treatment process through a series of chain degradation reactions, which helped to prevent azide compounds from forming in the combined oxidation systems due to cross oxidation of UDMH. Limited by costs and in consideration of the synergistic effect of H₂O₂, O₃ and UV in the next step, the optimal pre-treatment conditions were that V , t_{pre} and D_{hyp} were 1.5 m³·min⁻¹, 6 h and 47.2 g·L⁻¹ separately.

3.2 Influence of UV

3.2.1 Influence of UV Wavelength Ratio

Different UV wavelength ratios will produce different synergies with O₃ and H₂O₂ in the system (Sekiguchi et al., 2007). In the experiment, UV light sources of 185 nm and 254 nm were combined to find out the optimal ratio. When t_{rea} is 60 minutes, the relation between different UV wavelength ratios and COD removal efficiency is shown in Figure 4.

As shown in the figure, when the ratio of UV of 185 nm to UV of 254 nm was 3:2, the COD removal efficiency was the highest. As the ratio of UV of single wavelength increased, the oxidation efficiency gradually decreased, for the catalytic efficiency of individual light was not as high as that of UV and O₃ and H₂O₂.

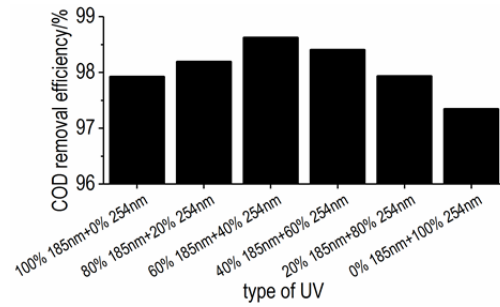


Figure 4: Influence of UV type on removal efficiency of COD.

3.2.2 Influence of UV Radiation Intensity

In order to maintain an uniform radiation, the UV radiation intensity is regulated by adjusting voltage. The influence of UV radiation intensity R on COD removal efficiency is shown in Figure 5.

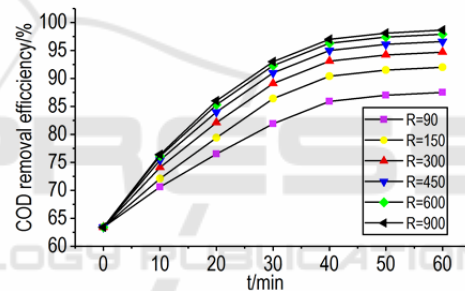


Figure 5: Influence of UV radiation intensity on removal efficiency of COD.

In the figure, the removal efficiency of COD increased as R increased, When R was 900 μW·cm⁻², COD removal efficiency could reach 98.62% after 60 min. In the oxidation system, O₃ and H₂O₂ could absorb UV to generate ·OH, while UV was the necessary promoter of ·OH in the system. Therefore, the higher the UV radiation intensity R is, the photons released will be more. Besides, more free radicals will be formed. Thus, it is necessary to keep the intensity of the ultraviolet radiation at the highest level that the amalgam lamp can achieve.

3.3 Influence of Ozone

In the absence of liquid flow, there was only gas flow in the whole process. According to Henry's law, the liquid mass transfer coefficient K_L can be derived as:

$$K_L \cdot \frac{\sigma}{d_b} \cdot \frac{Q_g}{V_b} \cdot (C_g \cdot HRT - C_{\text{ozone}}) = -Q_g \cdot \frac{dC_g}{dh} = K_L \cdot C_{\text{ozone}} \cdot A \quad (1)$$

Applying the boundary conditions ($y=0$, $C_g=D_{\text{ozone}}$), the analytical solution of liquid ozone concentration C_{ozone} in steady state can be obtained:

$$C_{\text{ozone}} = \frac{\sigma \cdot K_L \cdot Q_g \cdot HR \cdot T_{\text{ozone}}}{\sigma \cdot K_L \cdot Q_g + K_L \cdot A \cdot V_b \cdot d_b} \cdot \exp\left(-\frac{\sigma \cdot K_L \cdot K_b \cdot A \cdot HR \cdot h}{\sigma \cdot K_L \cdot Q_g + K_L \cdot A \cdot V_b \cdot d_b}\right) \quad (2)$$

Where:

- K_L — Liquid mass transfer coefficient, $\text{m} \cdot \text{s}^{-1}$;
- σ — The surface tension of water, $0.071 \text{ N} \cdot \text{m}^{-1}$ for tap water;
- d_b — The average diameter of bubble, m ;
- Q_g — Intake air flow, $\text{m}^3 \cdot \text{s}^{-1}$;
- V_b — Bubble rise speed, $\text{m} \cdot \text{s}^{-1}$;
- C_g — Gas - phase ozone concentration, $\text{mol} \cdot \text{L}^{-1}$
- H — Henry constant, $\text{mol} \cdot (\text{L} \cdot \text{pa})^{-1}$;
- R — Universal constants, $8.314 \text{ J} \cdot (\text{mol} \cdot \text{K})^{-1}$;
- T — Reaction temperature, K
- C_{ozone} — Liquid ozone concentration, $\text{mg} \cdot \text{L}^{-1}$;
- h — Bubble height, m ;
- A — Reactor cross-sectional area, m^2 .

If the self-attenuation coefficient of ozone can be neglected ($K_d=0$) after the steady state was reached, equation (2) can be simplified as:

$$C_{\text{ozone}} = D_{\text{ozone}} \cdot HRT \quad (3)$$

In other words, the ozone concentration in the reaction system is determined only by D_{ozone} , Henry constant and T , regardless of the reactor size, inlet flow rate, bubble particle size and other factors (Xu et al., 2016).

Therefore, in the experiment, when Henry constant and T are unchanged, only the impact of D_{ozone} on the degradation of COD in waste water will be studied. It is shown in Figure 6.

In the combined oxidation system, UDMH and its intermediates are mainly oxidized by $\cdot\text{OH}$. Under UV irradiation, O_3 reacts with H_2O to produce H_2O_2 , while H_2O_2 absorbs UV to produce $\cdot\text{OH}$. O_3 can also react with H_2O_2 or H_2O to generate $\cdot\text{OH}$. As D_{ozone} increases, the amount of $\cdot\text{OH}$ produced in the system gradually increases as well, which results in a higher COD removal efficiency.

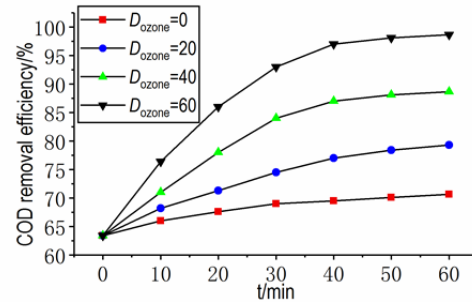


Figure 6: Influence of Dozone on removal efficiency of COD.

3.4 Influence of Initial Concentration

The influence of initial UDMH concentration on COD removal efficiency is shown in Figure 7.

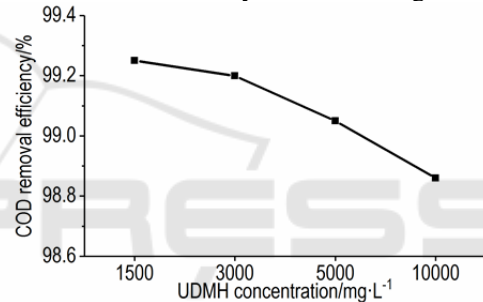


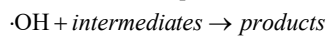
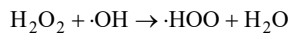
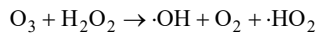
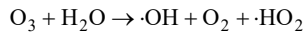
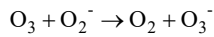
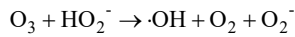
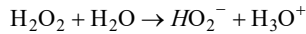
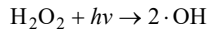
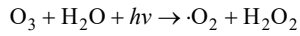
Figure 7: Influence of concentration of UDMH on removal efficiency of COD.

As the initial concentration increased, the COD removal efficiency decreased step by step, but the absolute amount of oxidized COD increased at a given time interval. When the initial concentration of UDMH increased from $1500 \text{ mg} \cdot \text{L}^{-1}$ to $10000 \text{ mg} \cdot \text{L}^{-1}$, the absolute amount of COD oxidized in 60 min changed from 4838.2 mg to 32132.1 mg. This phenomenon may be resulted from the formation of intermediates, which acted as a hydroxyl radical scavenger at the beginning when the concentration of UDMH was high, thereby reducing the rate of oxidation reaction.

3.5 Synergistic Effect of the System

In the system, H_2O_2 can be used as initiator and accelerator for O_3 hydrolysis (Alkandari et al., 2016). UV of 254 nm can lead to the decomposition of H_2O_2 (Minamidate et al., 2006). UV of 185 nm can decompose O_2 in water to produce O_3 and promote the hydrolysis of O_3 (Lekkerkerker et al., 2012).

Specific synergies can be expressed briefly as follows:



3.6 Kinetics of Reaction

According to the data in Fig.2 to Fig.7, H₂O₂/UV/O₃ combined oxidation process of UDMH conforms to the quasi-first order reaction kinetics process, and the apparent quasi-first order reaction kinetics equation applies to the degradation of UDMH through the above process:

$$-\ln(C / C_{\text{UDMH}}) = k_{\text{obs}} \cdot t \quad (4)$$

C in equation (4) represent the concentration of UDMH when reaction time is t , k_{obs} is the quasi-first order reaction kinetics constant. UDMH concentration during the reaction, hydrogen peroxide dosage, UV radiation intensity and ozone dosage rate are the vital factors to degradation effect. So, equation (4) can be expressed as:

$$k_{\text{obs}} = \varepsilon \cdot C_{\text{UDMH}}^a D_{\text{hyp}}^b R^c D_{\text{ozone}}^d \quad (5)$$

ε , a , b , c , d are constants and can be obtained from the lg-lg diagram of the experimental data. According to equation (4), (5) and experimental data, the kinetic equation of the reaction can be written as:

$$k_{\text{obs}} = 3.7 \times 10^3 \cdot C_{\text{UDMH}}^{-0.0021} D_{\text{hyp}}^{0.0913} R^{0.0509} D_{\text{ozone}}^{0.1947} \quad (6)$$

From equation (6), it can be seen that the ozone dosing rate D_{ozone} and the UV radiation intensity R have a great influence on the oxidation rate constant of UDMH. With the increase in D_{ozone} and R , the rate constant increases almost linearly. The UDMH concentration C_{UDMH} has a little negative effect on rate constants which is negligible.

4 CONCLUSIONS

(1) With a proper UV wavelength ratio, the degradation rate of UDMH in waste water positively correlated with the dosage of hydrogen peroxide,

aeration rate of pre-treatment, pre-treatment time, ultraviolet radiation intensity and ozone dosing rate. But the concentration of UDMH had little negative influence on it.

(2) The optimum conditions were as follows: the reaction temperature $T=30.0$ °C, pH=9.0, the pre-treatment parameters $D_{\text{hyp}}=47.2$ g·L⁻¹, $V=1.5$ m³·min⁻¹, $t_{\text{pre}}=6$ h, radiation intensity 900 μW·cm⁻², ratio of 185 nm ultraviolet light sources to 254 nm ones 3:2, ozone dosing rate 60 mg·(L·min)⁻¹, the reaction time 60 min the concentration of waste water 5000 mg·L⁻¹. UDMH and COD removal efficiencies can reach 100% and 98.62% separately under the conditions above.

(3) The H₂O₂/UV/O₃ combined oxidation system has a more significant synergistic effect than individual oxidation systems. The cause for the synergic effect is the initial ultraviolet radiation on the hydrolysis of ozone and hydrogen peroxide as well as ozone decomposition resulted and promoted by hydrogen peroxide in the reaction process.

(4) The H₂O₂/UV/O₃ combined oxidation process conforms to the quasi-first order reaction kinetics process. The kinetic equation can be written as: $k_{\text{obs}} = 3.7 \times 10^3 \cdot C_{\text{UDMH}}^{-0.0021} D_{\text{hyp}}^{0.0913} R^{0.0509} D_{\text{ozone}}^{0.1947}$, The ozone dosage rate and the UV radiation intensity R have a great influence on the UDMH oxidation rate constant.

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