# Indication of Solution Temperature and Conductivity During Electrochemical Oxidation of Hydrazine Wastewater

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Abstract: The electrochemically activated persulfate process has been demonstrated to enhance the efficacy of the degradation of unsymmetrical dimethylhydrazine (UDMH) in wastewater. The concentration of UDMH was typically determined through amino sodium ferrocyanide spectrophotometry. Nevertheless, the lengthy chromogenic reaction time and intricate operational procedure impede the efficiency of the analysis. The utilization of solution conductivity and temperature as indicators to ascertain the extent of UDMH degradation can enhance the efficiency of the analytical process. The impact of varying voltage, initial pH, ionic strength, $Na_2S_2O_8$ dosage, circular flow, and UDMH concentration on the observed patterns of UDMH concentration, pH, solution temperature, and conductivity were investigated. A correlation was identified between the transition points for the rapid and gradual changes in conductivity and temperature, which occurred five minutes earlier than those observed in the UDMH concentration and pH. During the sampling process, the degree of UDMH removal can be predicted online by monitoring the solution temperature and conductivity, thereby reducing the duration of the test and enhancing the efficiency of the analysis.

## 1 INTRODUCTION

The generation of propellant wastewater from rocket launches is a significant environmental concern. Each launch produces over 300 tons of wastewater (Li et al., 2017), with high-density launches generating even greater quantities. This wastewater has the potential to overwhelm wastewater treatment systems and negatively impact the surrounding ecological environment at satellite launch centers. While the advent of novel green propellants, such as liquid hydrogen and liquid oxygen, has mitigated the environmental impact, conventional propellants, particularly unsymmetrical dimethylhydrazine (UDMH), retain a pivotal role in thruster attitude adjustment (Zheng et al., 2006). UDMH is classified as a Class II highly toxic substance, and it has the potential to cause a deficiency of vitamin B6, which can lead to disease. Furthermore, it has been identified as a teratogenic, carcinogenic, and mutagenic hazard to humans (Zeng et al., 2019a; Deng et al., 2015).

The current treatment methods for UDMH can be broadly classified into the following categories: adsorption, ion exchange, biological treatment, advanced oxidation processes, and so forth. In a study conducted by (Gu et al., 2019), UDMH was adsorbed using oxalic acid-modified attapulgite, resulting in an adsorption efficiency of 95%. Nevertheless, the adsorption method is primarily applicable to the treatment of propellant wastewater with low concentration and significant fluctuations in water quality (Gu et al., 2019). Li et al. (2006) synthesized a strong acid cation exchange fiber, which demonstrated a treatment capacity that was 3.86 times greater than that of 732 strong acid cation exchange resin. Nevertheless, the ion exchange capacity is susceptible to interference from background hardness ions, and the regeneration rate is relatively slow (Deng et al., 2015). Wang (2005) achieved 98% removal of UDMH and 89% removal of $COD_{Cr}$ through the domestication of activated sludge. However, this method has a complex microbial cultivation process and a lengthy degradation reaction time, which restricts its promotion and application. Zeng's team prepared nitric acid-modified $g\text{-}C_3N_4$

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(Zeng et al., 2019b), $TiO_2$/g-$C_3N_4$ (Zeng et al., 2018), and modified $TiO_2$/g-$C_3N_4$ (Zeng et al., 2019a), which demonstrated a notable degradation effect on UDMH. Hou et al. (2019) employed a near-critical water oxidation process to facilitate the harmless treatment of high-concentration UDMH waste liquid.

Plasma is the fourth state of matter, occurring when gases are ionized to a sufficient extent. It can be produced either completely or partially, and only under specific conditions. The process of high-pressure discharge results in the formation of a considerable number of free electrons, which are subsequently accelerated to attain a high level of energy. Ultraviolet light irradiation, shockwaves and other physicochemical effects are produced by high-energy electrons and non-elastic collisions between atoms or molecules. The prevailing hypotheses regarding the mechanisms by which plasma removes water pollutants are as follows: high-energy electron action, ozone oxidation, and ultraviolet light radiation. The utilization of plasma in wastewater treatment offers a number of advantages, including a compact structure, a small footprint, convenient operation, wide adaptability to raw water, the absence of the need to add chemicals during the reaction process, and the absence of risk of secondary pollution.

Qiu et al. (2020) employed nanosecond pulse power to achieve the degradation of 83.2% of acid red 73 dyes. Rong et al. (2020) applied low-temperature plasma to treat polyacrylamide, achieving a degradation rate of 85.74%. Liu et al. (2020) exploited the strong reductive ·H and oxidative ·OH generated during low-temperature plasma discharge to achieve the simultaneous reduction of Cr(VI) and oxidation of phenol. Yi et al (2019) utilized dielectric barrier discharge low-temperature plasma to achieve the degradation of 82.1% of UDMH. Nevertheless, the fundamental theory and empirical findings pertaining to the utilization of plasma for the remediation of hydrazine propellants are comparatively scarce within both domestic and international academic circles. Furthermore, the direct application of plasma in industrial wastewater treatment is characterized by high energy consumption and a low energy throughput, which constrains the practical deployment of this technology (Wu et al., 2019).

The Fenton-like advanced oxidation technology based on sulfate radicals has recently attracted attention due to several favorable characteristics. Its oxidation-reduction potential (2.5-3.1 V) is higher than that of ·OH (1.8-2.7 V), the half-life of $\cdot SO_4^-$ is long and difficult to affect by pH, and it has strong oxidation selectivity. At room temperature, the oxidizing power of persulfate is limited and requires activation by an activator to produce $\cdot SO_4^-$. The activation of persulfates can be achieved through the application of ultraviolet visible light, heat, alkali, microwave radiation, carbon materials, and transition metals. Of these, ultraviolet light radiation and heat produced under plasma action have been demonstrated to be particularly effective in this regard.

Based on this, the combination of plasma and persulfate to remove UDMH can be used to activate persulfate, producing ·OH and $\cdot SO_4^-$, in two ways. Firstly, ultraviolet light and heat produced by plasma can be used to activate persulfate. Secondly, ozone and high-energy electrons formed by plasma discharge enable direct attack on pollutants. This approach allows the complementary advantages of both methods to be achieved.

In the preceding stage, the parameters, including voltage, initial pH, background ion concentration, persulfate dosage, circulation flow rate, and pollutant concentration, were optimized to identify the optimal operating conditions for the process (Zhou et al., 2023). These conditions were found to result in a 93.8% removal efficiency for 100 mg/L UDMH. However, the measurement of UDMH concentration in the effluent was obtained by the GB/T 14376-1993 amino ferrocyanide sodium spectrophotometry method, which has a lengthy coloration reaction and complex operational steps. Accordingly, we explored the potential of utilizing convenient test indicators as proxies for the degree of reaction, with a view to employing them as alternative indicators for UDMH concentration. In this regard, we examined the fluctuations in solution temperature and conductivity throughout the UDMH treatment process.

# 2 METHOD

## 2.1 Reagents

$Na_2S_2O_8$, NaCl, NaOH, $HgSO_4$, $Ag_2SO_4$, $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$, $Na_2HPO_4\cdot 12H_2O$, $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, 1,10-phenanthroline, acetic acid, acetylacetone, ammonium acetate were all purchased from the National Pharmaceutical Group, analytical pure. $K_2Cr_2O_7$ was provided by the National Pharmaceutical Group as a guarantee reagent. Anhydrous ethanol, citric acid, 95-98% $H_2SO_4$ were provided by the Beijing Chemical Factory. UDMH was provided by the Beijing Aerospace Test Technology Research Institute (98.7%), and all steps involving the dilution, degradation, and analysis of UDMH were carried out in a fume hood. All reagents were dissolved and diluted with ultrapure water prepared by Milli-Q (18.2 MΩ, USA) and stored in a refrigerator set at 4°C after preparation.

## 2.2 Experimental Apparatus

The entire experimental system consists of the following components: a tubular reactor, a blower, a power supply, an oscilloscope (MSO7104B, Agilent Technologies), a peristaltic pump (LongerPump), a water tank, and so forth. The UDMH solution in the water tank is forced into the inlet by the peristaltic pump (LLS PLUS-B163, Kachuaner Fluid Technology Co., Ltd.), enters the quartz inner tube from the bottom, overflows from the top of the inner tube, and enters the gap between the inner and outer tubes. Upon traversing the 110 mm-long discharge zone, the wire mesh assumes the role of the high-voltage pole, while the UDMH wastewater serves as the ground pole. The treated solution is then conveyed to the lower water tank, where it is subjected to a further treatment cycle via the peristaltic pump. During the sampling process, it is essential to ensure that the power supply is deactivated and that the reaction is terminated with the addition of 0.1ml of anhydrous ethanol. The pH, conductivity, and solution temperature of the samples should be measured. Once the experiment has concluded, the liquid in the central tube should be emptied, rinsed with ultrapure water on several occasions and the remaining water should be drained away. The concentration of UDMH in the solution is determined by the GB/T 14376-1993 amino ferrocyanide sodium spectrophotometry method, with the measurement instrument being the SHIMADZU UV-2550 spectrophotometer. Meanwhile, the temperature and conductivity are recorded with the HACH HQ14d apparatus.

# 3 RESULTS AND DISCUSSION

## 3.1 Influence of Initial pH

Changing the pH of the solution will change the form of existence of UDMH, and it is necessary to study the changes in solution temperature and conductivity under different pH conditions. Degradation of 100 mg/L UDMH waste water under the environment of maintaining a NaCl background ionic strength of 50 mmol/L, a discharge voltage of 12.5 kV, a $Na_2S_2O_8$/UDMH (mol/mol) ratio of 1.0 and a circulation flow rate of 140 mL/min.

The change in conductivity of the solution is shown in Figure 1. As can be seen from the figure, the solution conductivity corresponding to the initial pH of 4-10 increases as the reaction time is increased, rising rapidly within the first 5 minutes and then slowing down.

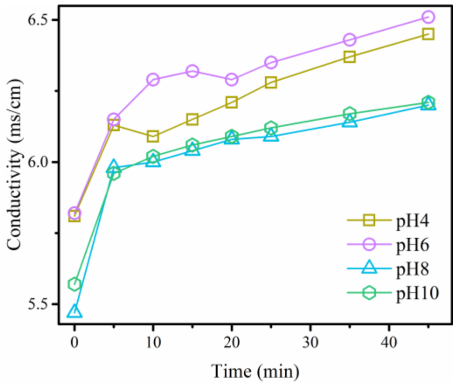

Figure 1: Conductivity variation with time as initial pH fluctuation.

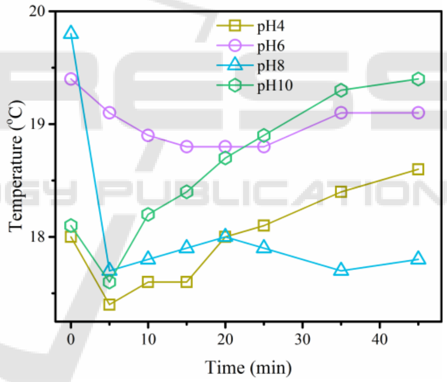

Figure 2: Temperature variation with time as initial pH fluctuation.

The change in solution temperature is shown in Figure 2. Except for the solution corresponding to the initial pH of 6, the solution temperature decreases rapidly within the first 5 minutes and then increases. When the initial pH is 6, the solution temperature decreases slowly and starts to increase after 25 minutes.

Compared with previously reported patterns of change in UDMH concentration and pH (Zhou et al., 2023), the rapid response phase of solution temperature and conductivity also appeared to precede the initial pH change by 5 min, i.e. the cut-off point between rapid and slow responses for solution temperature and conductivity was 5 min, and

10 min was used as the cut-off point between rapid and slow responses for UDMH concentration and pH.

## 3.2 Influence of Background Ion Concentration

The changes in solution temperature and conductivity were investigated as the background ionic strength of NaCl was varied at a molar ratio of $Na_2S_2O_8$ to hydrazine hydrate of 1.0, an initial pH = 8, a discharge voltage of 12.5 kV, a recirculation flow rate of 140 mL/min and an initial concentration of meta-dihydrazine of 100 mg/L.

The change in conductivity of the solution is shown in Figure 3. As can be seen from the figure, the solution conductivity corresponding to 0 mM and 50 mM NaCl increases as the reaction time is increased, rising rapidly within the first 5 minutes and then slowing down. In contrast, the conductivity of the solution corresponding to 100 mM NaCl decreases rapidly during the first 10 minutes and then increases slowly. The rapid decrease in conductivity is due to the high concentration of $Cl^-$ which is rapidly oxidized and gasified in the electrochemical reaction.

The variation in solution temperature is shown in Figure 4. The solution temperature decreased rapidly for the first 5 min, then the solution temperature increased. The solution temperature increased linearly with the fastest growth at 0 mM NaCl background ionic strength. The increase in temperature may be due to the low conductivity and high resistivity of the solution resulting in high heat generation.

Similarly, the cut-off points for fast and slow solution temperature, conductivity were 5 min earlier than the cut-off points for fast and slow UDMH concentration, acidity and alkalinity as the background ionic strength was varied.

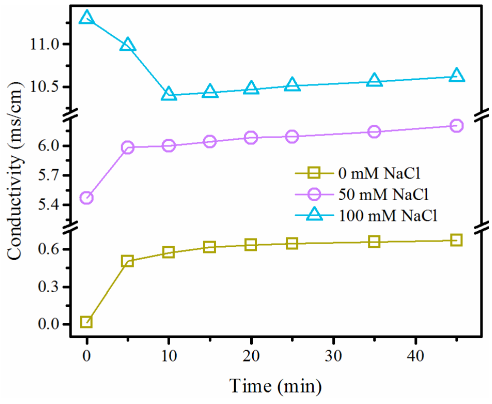

Figure 3: Conductivity changing with time as NaCl concentration fluctuates.

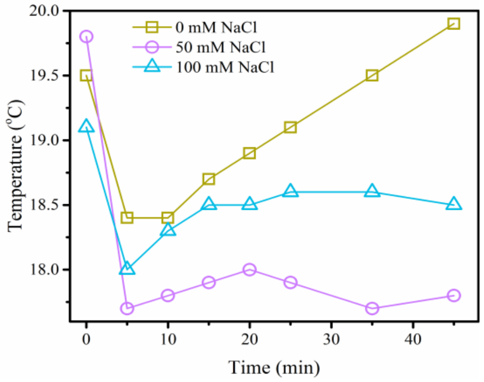

Figure 4: Temperature changing with time as NaCl concentration fluctuates.

## 3.3 Influence of $Na_2S_2O_8$ Dosage

Optimization of $Na_2S_2O_8$ as a key factor in the degradation of UDMH wastewater is necessary. UDMH effluent of 100 mg/L was degraded by maintaining the initial pH = 8, a recirculation flow rate of 140 mL/min, a background NaCl ionic strength of 50 mmol/L and a loaded voltage environment of 12.5 kV.

The variation in solution conductivity is shown in Figure 5. As can be seen from the figure, without $Na_2S_2O_8$ the solution conductivity decreased slightly in the first 10 minutes and then slowly increased. After the addition of $Na_2S_2O_8$, the solution conductivity increased rapidly in the first 5 minutes and then the growth rate slowed down.

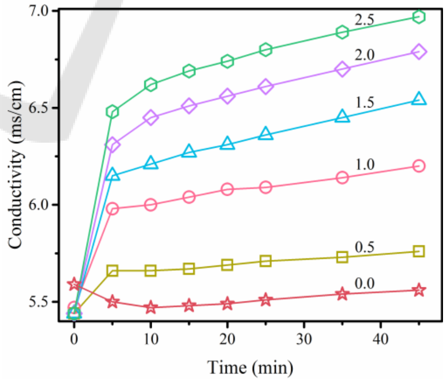

Figure 5: Conductivity changing with time as $Na_2S_2O_8$ fluctuates.

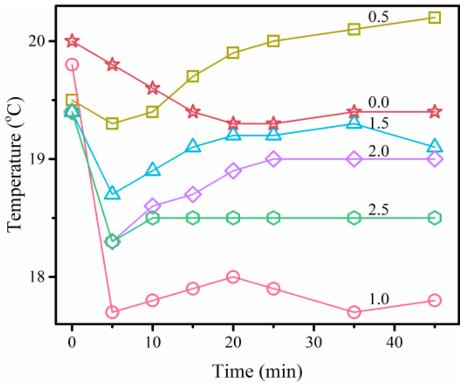

Figure 6: Temperature changing with time as $Na_2S_2O_8$ fluctuates.

The variation of the solution temperature is shown in Figure 6. After the addition of $Na_2S_2O_8$, the solution temperature decreased for the first 5 minutes, after which the solution temperature increased. In contrast, when $Na_2S_2O_8$ was not added, the solution temperature continued to decrease slowly and then reached a steady state.

The cut-off point for fast and slow solution temperature and conductivity was 5 min when $Na_2S_2O_8$ dosage was varied.

### 3.4 Influence of Circulation Flow Rate

The influence of the circulation flow rate on the solution temperature and conductivity was investigated under the conditions of maintaining an initial pH of 8, a NaCl background ionic strength of 50 mmol/L, a $Na_2S_2O_8$/UDMH (mol/mol) ratio of 2.0 and a voltage of 12.5 kV.

The variation of the solution conductivity is shown in Figure 7. As can be seen from the figure, the solution conductivity corresponding to the three different recirculation flow rates all increased with reaction time. The conductivity increased rapidly in the first 5 min and then the growth rate slowed down and the final conductivity followed the pattern of the UDMH removal rate, reaching a maximum value at 140 mL/min.

The variation in solution temperature is shown in Figure 8. 140 mL/min and 180 mL/min correspond to solutions with a rapid decrease in temperature during the first 5 min, after which the solution temperature increases. In contrast, the temperature of the solution corresponding to 100 mL/min decreased continuously.

The cut-off point for the fast and slow changes in solution temperature and conductivity is 5 minutes when the cyclic flow rate is varied.

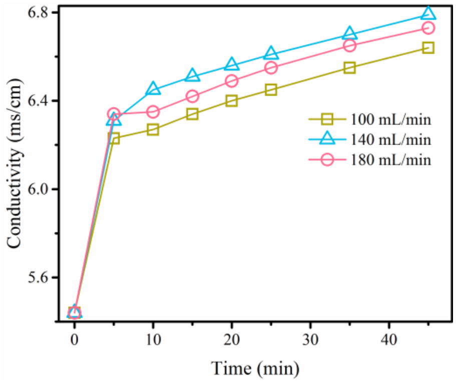

Figure 7: Conductivity changing with time as circular flow fluctuates.

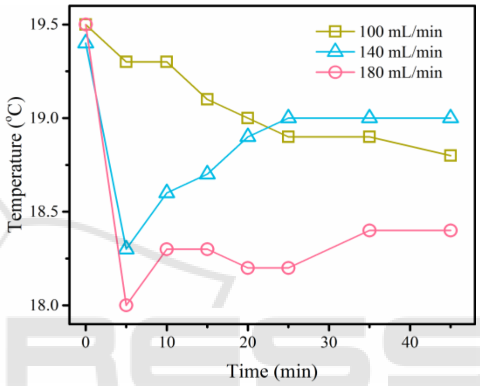

Figure 8: Temperature changing with time as circular flow fluctuates.

### 3.5 Influence of UDMH Concentration

The effects of fluctuations in the initial concentration of UDMH on the temperature and conductivity of the solution were investigated under the environment of maintaining the initial pH = 8, circulating flow rate of 140 mL/min, NaCl background ionic strength of 50 mmol/L, $Na_2S_2O_8$/UDMH (mol/mol)=2.0 and loading voltage of 12.5 kV, and the results are shown in Figures 9-10.

The variation of the solution conductivity is shown in Figure 9. As can be seen from the figure, the solution conductivities corresponding to the three different initial UDMH concentrations all increased with reaction time, with a rapid increase in conductivity in the first 5 minutes and a slower rate of increase thereafter.

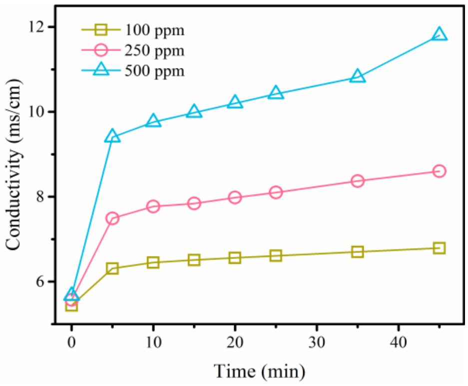

Figure 9: Conductivity variation with time as UDMH concentration fluctuates.

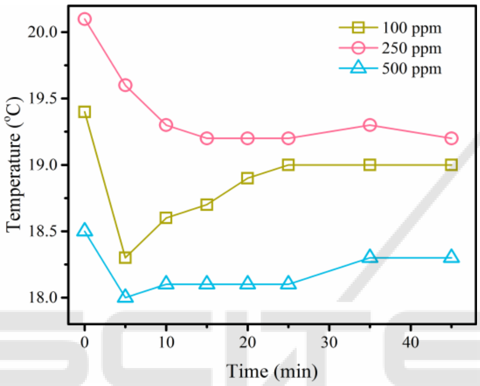

Figure 10: Temperature variation with time as UDMH concentration fluctuates.

The changes in solution temperature are shown in Figure 10. 100 ppm and 500 ppm correspond to solutions with a rapid decrease in temperature during the first 5 minutes, after which the solution temperature increases. In contrast, the temperature of the solution corresponding to 250 ppm continued to decrease.

The cut-off point for the fast and slow changes in solution temperature and conductivity is 5 min when the initial concentration of UDMH is changed.

## 4 SUMMARY

In order to solve the problems of long colour development reaction time and complicated operation steps of spectrophotometric measurement of UDMH concentration, the conductivity and temperature of the solution, which are convenient for testing, were used as the indicators to judge the degree of electrochemical degradation of UDMH. During the degradation of UDMH wastewater by $Na_2S_2O_8$ synergistic plasma, when the variables such as voltage, initial pH of solution, background ion concentration, $Na_2S_2O_8$ dosage, recycle flow rate, and initial concentration of UDMH were changed, the change rules of the UDMH concentration, acidity and alkalinity with the temperature of the solution, and the electrical conductivity were checked in turn, and the results showed that: under different reaction conditions, the change of the UDMH concentration and the acidity and alkalinity were fast and slow. The results showed that under different reaction conditions, the cut-off point of UDMH concentration, acidity and alkalinity appeared at 10 min, and the corresponding transition point of solution temperature and conductivity was 5 min. Based on this, the transition point of UDMH rapid degradation to slow degradation can be predicted online by collecting the solution temperature and conductivity during the sampling process, so as to shorten the duration of the test and improve the efficiency of the test.

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